Renewable and Sustainable Energy Reviews 22 (2013) 46–72

Contents lists available at SciVerse ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Advances in diesel–alcohol blends and their effects on the performance and emissions of diesel engines

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ARTICLE INFO

Article history:
Received 7 August 2012
Received in revised form
8 January 2013
Accepted 14 January 2013
Available online 28 February 2013

Keywords:
Diesel fuel
Bio-alcohols
Alternative fuel
Engine emissions
Engine performance

ABSTRACT

The increasing energy demand, surging oil prices, depleting oil reserves and environmental pollution problems associated with the use of fossil fuels have sparked renewed interest to find out clean alternative fuels. Alcohols such as methanol, ethanol and butanol are competitive alternative fuels due to their liquid nature, high oxygen contents, high octane number and their production from renewable biomass. In this review, the fuel properties of these alcohols are compared with conventional gasoline and diesel fuel. The comparison of fuel properties represents that butanol has the potential to overcome the problems associated with the use of methanol and ethanol. Progresses of their production from different sources are also introduced. Further, several techniques such as alcohol–diesel fuel blends and alcohol–diesel fuel emulsions are discussed, especially for lower alcohols, in order to use them in diesel engines. The effects of diesel–alcohol blends on the combustion, performance and emissions of diesel engines are also analyzed. It is examined that blending of alcohols, along with some CN improver, to diesel fuels can reduce diesel engine emissions without adverse impacts on the performance of diesel engines. These studies also reveal that butanol is a better alternative for diesel fuel due to its superior fuel properties and miscibility with diesel fuel than those of methanol and ethanol. Finally, some critical conclusions and future research directions are highlighted.

Contents

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1364-0321/$ - see front matter
http://dx.doi.org/10.1016/j.rser.2013.01.017

1. Introduction

Owing to their excellent drivability and fuel economy, diesel engines are the most common internal combustion (IC) engines that are widely used in various sectors such as agriculture, transportation and industry. Their use is expected to become more widespread in the foreseeable future. Diesel engines produce smaller volumes of carbon monoxide (CO), hydrocarbons (HC) and carbon dioxide (CO_2) than gasoline-powered engines, mainly due to the lean nature of diesel–air mixtures (which results in cooler combustion) and good fuel efficiency; however, diesel engine emissions contain comparatively high levels of nitrogen oxides (NO_x) and particulate matter (PM) [1]. The absolute contribution of diesel vehicles to total pollutants and greenhouse emissions has been growing due to their increasing numbers in fleets and increasing distances traveled [2]. Air pollution causes serious health problems, especially respiratory and cardiovascular problems. Increasing global anxiety about combustion-related pollutants, such as THC (total hydrocarbon), NO_x, SO_x (sulfur oxides), CO, CO_2, acid rain and photochemical smog, as well as depletion of the ozone layer, has led many nations to control emissions and implement initiatives to control pollution. In addition, current petroleum reserves are projected to deplete in the near future [3].

Due to these growing concerns studies on the applicability of clean energy technologies continue to receive attention. Hence, stricter diesel fuel standards have been announced to decrease NO_x, particulate and CO_2 emissions, and fuel consumption [1]. In addition, the search for sustainable alternative fuels such as alcohols, biodiesel and ethers for diesel engines has recently become important. In order to meet the increasing energy demand and control the environmental pollution, it is important to adopt a sustainable policy that allows the substitution of diesel fuel by neat biofuels such as biodiesel, biomethanol, bioethanol, biobutanol or blends of such biofuels with diesel fuel. Furthermore, studies dedicated to the reduction of emissions by diesel vehicles have shown that modifications of the specifications of commercial diesel fuel are required to decrease and optimize emissions from diesel engines [1].

The mixing of oxygenated additives with diesel oil supplies the oxygen required to form CO_2 instead of carbon-rich particles. This in turn may considerably reduce PM emissions [4–6]. The use of oxygenates as fuel additives to facilitate cleaner burning of petroleum fuels is half of a century old [7]. Since its introduction, many investigators have studied the impact of blending various oxygenates with diesel fuel. The most commonly investigated oxygenated additives are alcohols [8–11] and methyl or ethyl esters (biodiesel) [8,12,13]. However, other oxygenated organic compounds (ethers, glycol ethers, and esters) have been investigated to examine the impacts of oxygen content on fuel properties, combustion and emissions. For example, Liotta et al. [14] examined the effects of oxygenated fuels such as glycol ethers, aromatic alcohol, aliphatic alcohol and polyether polyol on emissions in a heavy duty diesel engine, and found that oxygen introduced by glycol ether addition was more effective in decreasing the PM than was oxygen addition using alcohol. Glycol ethers were found to have positive impacts on diesel fuel properties and to reduce smoke opacity, CO, PM and NO_x emissions [5,15,16].The application of biodiesel has been found to decrease the smoke, PM and HC emissions while NO_x emissions increased. Moreover, acetoacetic esters and dicarboxylic acid esters [17], ethylene glycol monoacetate [18], 2-hydroxy-ethyl esters [19], 1-octylamino-3-octyloxy-2-propanol and N-octylnitramine [7], dimethoxypropane, dimethoxyethane [11] and dimethyl ether (DME) [20] were also found to have significant impacts on fuel properties, diesel fuel combustion and emissions. The addition of ethylene glycol monoacetate to diesel fuel caused an increase in BSFC (brake specific fuel consumption) and NO_x, CO and CO_2 emissions, while the PM and smoke emissions were decreased [18]. Using current engine technologies, DME was found to produce less greenhouse gas emissions than biodiesel, methanol and ethanol, while HC emissions were increased [20]. However, the use of DME in diesel engine causes a premature wear problem and subsequently the failure of pump and fuel injectors. Furthermore, the production cost of DME is higher due to the feedstock cost (natural gas) [20].

Moreover, the blending of alcohols such as methanol, ethanol and butanol was also found to have significant effects on the fuel properties, combustion and emissions of diesel fuels. The effects of these blends in terms of emissions are almost comparable with ethers, esters and other oxygenates. These blends also significantly decrease the exhaust emissions [21] and enhance octane number when mixed into diesel fuel. Such enhancement is particularly important in unleaded fuels. In addition, due to their complete burning power, alcohols have the potential to increase combustion efficiency. Therefore, the blends of alcohols (methanol, ethanol and butanol)–diesel oil with and without cetane number (CN) improver are potential alternative fuels.

Moreover, these alcohols can be produced from biomass resources. As a renewable resource, biomass represents a possibly endless source of feedstock for the production of biofuels. Nowadays butanol is normally synthesized from petroleum sources, but early butanol production was reported to use biological sources. In the first half of the 20th century, the commercial production of butanol from biomass was prominent, and this is what today's butanol users are anticipating to ensue again [22]. *n*-Butanol is a type of primary alcohol that has advantages over methanol and ethanol for use as an alternative fuel in IC engines, since most of the fuel properties of *n*-butanol are more similar to diesel fuel.

During the 1970s, despite their limited solubility and stability with diesel fuel, low CN and high hygroscopicity, methanol and ethanol were considered the best diesel fuel additives because of their accessibility, low cost, high oxygen contents, and suitability for use in diesel engines without modifications [23,24]. However, when these blends were later found to exhibit phase separation at certain compositions or as the temperature was reduced [25,26], thereby forming methanol/ethanol-rich bottom phases that could stall engines and prevent normal operation; many investigations were initiated to address these problems. One possible solution is using additives that are capable of increasing the solubility, stability and CN of methanol/ethanol–diesel fuel blends. Oxygenated compounds (fuel additives) have been distinguished to increase the miscibility of methanol/ethanol in diesel fuel and can reduce the particulate emissions from internal combustion engines, and further decline of particulate emissions using these additives depends on the molecular configuration and amount of oxygen in the fuel [27].

Because of their comparable fuel properties with diesel fuel and potential to be used in CI engines in pure form or blended

Nomenclature

BSFC	brake specific fuel consumption (g/kW h)
BSHC	brake specific unburned hydrocarbon (g/kW h)
BTE	brake thermal efficiency (%)
BSEC	break specific energy consumption (MJ/kWh)
BMEP	brake mean effective pressure
BTDC	Before top dead center
CI	compression ignition
IC	internal combustion
DI	direct-injection
IDI	indirect-injection
CNG	compressed natural gas
LNG	liquefied natural gas
THC	total hydrocarbons
UHC	unburned hydrocarbon
HC	hydrocarbon
CO	carbon monoxide (% volume)
CO_2	carbon dioxide (% volume)
HC	hydrocarbon (ppm volume)
NO	nitric oxide (ppm volume)
NO_x	nitrogen oxides (ppm volume)
SO_x	sulfur oxides
$T_{exhaust}$	exhaust gas temperature (°C)
P_{max}	maximum cylinder pressure
TPA	tone per annum
MT	million tones
BTU	British thermal unit
ABE	acetone–butanol–ethanol
rpm	revolutions per minute
CN	cetane number
EGR	exhaust gas recirculation
ORG	original
LHV	lower heating value
LTC	low-temperature combustion
DOC	diesel oxygen catalyst
ULSD	ultralow sulfur diesel
LSD	low sulfur diesel
DMCC	diesel methanol compound combustion
TDI	turbo charged direct injection
SFC	specific fuel consumption
HDDI	heavy duty direct injection
MeCHO	acetaldehyde
HCHO	formaldehyde
HSD	high speed diesel fuel

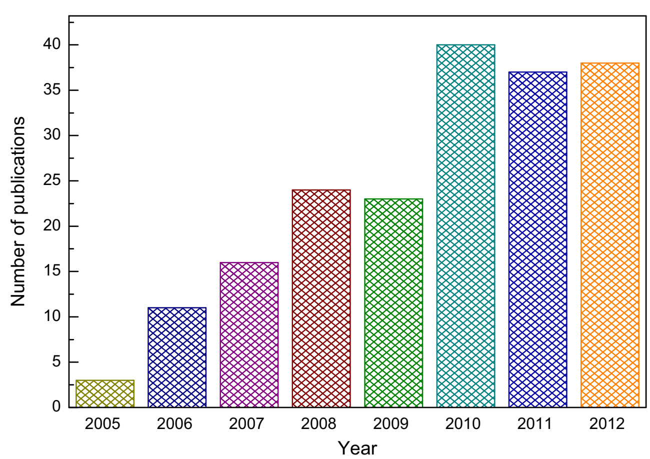


Fig. 1. Publications addressing diesel–alcohol blends from 2005 to 2011 (Scopus database).

with conventional diesel fuel [28–31], it is anticipated that alcohols will be able to slow down the worldwide petroleum consumption and decrease the level of dependence on petroleum fuels.

Although the applications and impacts of alcohol–diesel fuel blends have been studied, further researches are required to optimize performance, guarantee conservation of engines in which such blends are applied, and develop appropriate distribution systems. Hence, substantial researches are required to assess the performance and emissions characteristics of diesel engines fueled with ethanol–diesel, methanol–diesel and butanol–diesel blends. The growing interests in alcohol additives for diesel fuel are evidenced by the number of related studies published between 2005 and 2012 (Fig. 1).

From 2005 to 2012, 186 (142 articles, 35 conference papers, 8 reviews and 1 business article) research studies have been published on the issue of diesel–alcohol blends. These publications focus on numerous aspects with the aim of making alcohol–diesel blends a next generation fuel. Some of the topics include alcohol sources, phase behavior and fuel properties of alcohol–diesel blends, effects of alcohol–diesel fuel blends on the performance and emissions of diesel engines, and the effects of injection timing and pressure on the exhaust emissions of diesel engines fueled with these blends.

The main purpose of the present study is to provide a comprehensive review of the literature related to the use of diesel–alcohol blends in diesel engines and their effects on the combustion, performance and emissions of diesel engines.

2. Physicochemical properties of methanol, ethanol and butanol

The use of alcohols as fuels for internal combustion engines is not a new innovation as these have been used since the invention of IC engines. Actually, the level of curiosity with regard to using alcohol as a motor fuel has followed cycles of fuel shortages and/or low food-grain prices. Alcohol may be blended with diesel fuel or gasoline to produce diesohol and gasohol respectively, or alcohol may be added to the air intake of the engine. The significant physicochemical properties of methanol, ethanol and butanol are discussed below.

2.1. Methanol

Methanol, commonly known as methyl alcohol, is the simplest alcohol, containing one carbon atom. It is a colorless, tasteless liquid with a very faint odor. It is a polar solvent and is miscible with water, alcohols, esters and most organic solvents, and is only slightly soluble in fats and oils. The flash, melting and boiling points of methanol are 12 °C, −97.8 °C and 64.7 °C, respectively. Methanol is flammable and may explode when exposed to flame [32].

Methanol is hygroscopic in nature and may absorb water vapor directly from the atmosphere. Adsorbed water can dilute the fuel value of methanol and may cause phase separation in methanol–diesel blends [33].

2.2. Ethanol

Ethanol is a flammable polar solvent and is miscible with water. It has a vapor density of 1.59, which indicates that it is heavier than air. Consequently, ethanol vapors do not rise, similar to gasoline vapors. The specific gravity of ethanol is 0.79, which indicates that it is lighter than water; however, it is water-soluble. The auto-ignition temperature, boiling point, flash point, and melting point of ethanol are 423 °C, 78 °C, 13 °C and −114 °C, respectively [34]. Ethanol is less toxic than gasoline and methanol, and is not carcinogenic. Like gasoline, the major risk when using methanol as a motor fuel is flammability. In pure form, ethanol burns without any smoke and it is difficult-to-see blue flame. In denatured form there is little to no smoke, but a slight orange flame may be visible [35]. Due to high octane number, ethanol is a good fuel for compression ignition (CI) engines [36].

2.3. Butanol

Butanol is a four-carbon atom alcohol that exists as four isomers: *n*-butanol CH_3-$CH_2CH_2CH_2OH$ (normal-butanol), 2-butanol $CH_3CH_2CHOHCH_3$ (secondary-butanol), *i*-butanol $(CH_3)_2CH_2CHOH$ (*iso*-butanol) and *t*-butanol $(CH_3)_3COH$ (*tert*-butanol). All of the isomers produce about the same energy, but the manufacturing methods for each are totally different. All four isomers have the same formulae and the same amount of heat energy but have different molecular structures that affect their properties. Despite their similar molecular weights and functional groups, they have different solubilities.

n-Butanol is a linear aliphatic alcohol. It is a colorless, flammable, slightly hydrophobic liquid with distinct banana-like aroma and strong alcoholic odor. Direct contact may result in irritation to the eyes and skin, and its vapors have an irritant effect on mucous membranes and a narcotic effect when inhaled in high concentrations. It is completely miscible with most common organic solvents, but only sparingly soluble in water.

iso-Butanol is a colorless liquid with sweet musty odor. It is miscible with all common organic solvents and only slightly soluble in water, while sec-butanol (2-butanol) is a flammable, colorless liquid that is slightly soluble in water and completely miscible with polar organic solvents.

t-Butanol (3-butanol) is a clear liquid with camphor-like odor. It is highly soluble in water and miscible with ethanol and diethyl ether. It has a tendency to be solid at room temperature (melting point slightly above 25 °C). Important properties of different butanol isomers are compared in Table 1 [37].

Table 1
Comparison of various physicochemical properties of different isomers of butanol.

Property	*n*-Butanol	*iso*-Butanol	2-Butanol	3-Butanol
Density at 20 °C (g/cm^3)	0.810	0.802	0.806	0.781
Boiling point (°C)	118	108	99	82
Water solubility (g/100 mL)	7.7	8.0	12.5	Miscible
Flash point (°C)	35	28	24	11

2.4. Methanol, ethanol and butanol vs. gasoline and diesel fuel

Physicochemical properties of methanol, ethanol and butanol are compared with those of gasoline and diesel fuels in Table 2 [38–41].

From Table 2 it is evident that: (I) butanol has lower hygroscopicity than methanol or ethanol, and is therefore less affected by weather changes, (II) butanol has a higher flash point than methanol or ethanol and is therefore safer than either of them, (III) butanol produces approximately 25% more energy(heating value) than methanol and ethanol, and can thus yield better mileage compared to lower carbon alcohols, (IV) butanol has a higher octane rating than methanol or ethanol, (V) butanol has a longer hydrocarbon chain than both methanol and ethanol, making it fairly non-polar, and thus it is more similar to gasoline than methanol or ethanol and is completely miscible with gasoline and diesel fuel. These properties make butanol a much safer fuel than methanol or ethanol, which can be distributed through existing fuel distribution and storage infrastructure (pipelines, storage tanks and filling stations) [42], while methanol and ethanol can only be blended just before use, (VI) butanol is less corrosive than methanol or ethanol, and (VII) due to their higher latent heat of vaporization compared to diesel fuel, methanol and ethanol offer a longer ignition delay period of combustion. Usually, the viscosity of alcohols increases as the length of their carbon chain increases, thus, the kinematic viscosity of butanol is twice that of ethanol and five to seven times that of gasoline [43].

2.5. Summary and future research directions

The reported physicochemical properties of methanol, ethanol and butanol demonstrate that methanol has the lowest combustion energy [44] of all fuels listed, and because of its highly polar nature, methanol does not mix with diesel fuel. In contrast, ethanol can be mixed with diesel fuel provided that there is a little water in the ethanol. Another problem impeding the

Table 2
Comparison of various physicochemical properties of methanol, ethanol and butanol with those of gasoline and diesel fuels.

Property	Methanol	Ethanol	Butanol	Diesel fuel	Gasoline
Density at 20 °C (g/ml)	0.7866	0.7851	0.8098	0.829	0.74–0.80
Boiling point, (°C)	65	78	117–118	187–343	27–225
Motor octane no	104	102	78	–	81–89
Research octane no	136	129	96	15–25	91–99
Cetane no	3.8	5–8	≈25	40–55	5–20
Energy density (MJ/L)	16	19.6	27–29	46	32
Energy content (Lower heating value) (MJ/kg)	20.1	26.9	33.1	42.8	43.1
Higher heating value (MJ/kg)	22.7	29.7	36.6	44.8	47.3
Heat of vaporization (MJ/kg)	1.2	0.92	0.43	0.23–0.60	0.36
Freezing point, (°C)	−97	−114	−89.3	−40–34	−40
Flash point (°C)	12	13	35	74	−42
Autoignition temp (°C)	463	423	397	235	257
Flammability limits, volume (%)	36	3.3–19	1.4–11.2	6	7.6
Solubility in 100 g of water	Miscible	Miscible	Immiscible	Immiscible	Immiscible
Viscosity (10^{-3} Pa s)	0.5445	1.078	2.593	–	0.24–0.32

addition of ethanol to diesel fuel is its low CN [45]. However, butanol can be blended with diesel fuel at any concentration and does not separate when mixed with water or at low temperature. In blends with diesel fuel, butanol tends to reduce the solidification temperature of the fuel at low temperatures. However, the main obstacle in using butanol as a blending component with diesel fuel is its low CN, which may diminish auto-ignition capability of the blend during combustion. Hence, to overcome problems associated with the use of methanol, ethanol and butanol, further studies are required to identify some suitable additives or CN improvers that can enhance their fuel properties in order to make such alcohols suitable for diesel engine use.

3. Global production of methanol, ethanol and butanol and their feedstock

Due to continuous escalation in the cost of crude oil, research into sustainable, economical and environment-friendly alternatives to fossil fuels is becoming more significant [46]. Biofuels are promising alternatives to petroleum-derived fuels, particularly biofuels produced from renewable resources via fermentation processes, such as biomethanol, bioethanol and biobutanol. Biofuels are usually considered as fuel additives rather than petroleum surrogates [47]. The global production of methanol, ethanol and butanol is discussed below.

3.1. Methanol

Methanol is also known as wood alcohol, since it was derived from wood before modern production technologies were developed in the 1920s. Sustainable technologies for producing methanol from biomass are currently economically unfeasible. Presently, methanol is produced from synthetic gas or biogas and is used as a fuel for IC engines. Methanol production is a cost-intensive chemical process. Therefore, under current production conditions, only waste biomass such as crop residues, forage, grass, crops, wood resources, forest residues, short rotation wood energy crops and lignocellulosic components of municipal wastes can be a viable feedstocks for bio methanol production [48]. As a renewable resource, biomass represents a potentially endless supply of feedstock for methanol production. During 2010 about 47 million metric tons of methanol was sold globally [49]. Global annual methanol production capacity is expected to reach 96.5 million tons in 2015 from the current 75.2 million tons (Fig. 2).

The major countries producing methanol from biomass by the end of 2003 were the USA, Canada, Japan, and Brazil [50]. However, in 2007 China became the world's foremost methanol producer and consumer, and is a leading user of methanol as a transportation fuel. China's methanol production capability increased from 6.16 million tons in 2003 to more than 20 million tons in 2008 and is anticipated to be 40 million tons by the mid of 2012 [51]. China has more than 140 methanol plants, and many of the smaller plants are closing as larger, facilities are being built [51].

Methanol is presently manufactured from syngas, natural gas, refinery off-gas, coal and petroleum but can also be produced using wood waste or garbage through partial oxidation reaction into syngas, and subsequently by catalytic transformation into biomethanol [52–54]. The addition of adequate amounts of hydrogen to syngas for transforming biomass carbon into methanol carbon facilitates methanol production at levels almost double those of methanol derived from similar amounts of biomass alone. The costs of current natural gas feedstocks are so high even after tax waivers that renewable methanol is unable to compete financially with other fuel sources.

Biomass and coal are potential fuel sources for gasification, further syngas production and methanol synthesis. The possibility of realizing such conversion has been recognized in a large scale system in which a product gas is initially obtained by pyrolysis and gasification of a carbonaceous material [53,54]. Methanol production from biomass consists of a series of production steps that secure the future energy supply chain.

Synchronized biomethanol production (by the hydrogenation of CO_2 formed during the fermentation of sugar juice), in parallel with the production of bioethanol, appears to be economically attractive in locations where hydroelectricity is of very low cost and surplus lignocellulosic residues are available. Most biomethanol production processes require additional oxygen as an intermediate for the conversion of biomass into a syngas (H_2/CO). Freely accessible supplies of hydrogen (H_2) and oxygen (O_2) can increase the total productivity of biomass-derived methanol.

Methanol can also be produced from CO_2 and water (H_2O) using sunlight [55], which may help to control the global warming and serve as a renewable source of energy. The price of methanol produced using this approach would be 1.22 USD/kg, which is higher than current market prices (0.48 USD/kg) but is competent to other renewable-resource-based alternatives. Further, advanced technologies are being developed and this may eventually result in the commercial viability of renewable methanol production.

3.2. Ethanol

Currently ethanol is one of the most popular alcohol-based fuel, as it is produced by the simple fermentation of natural

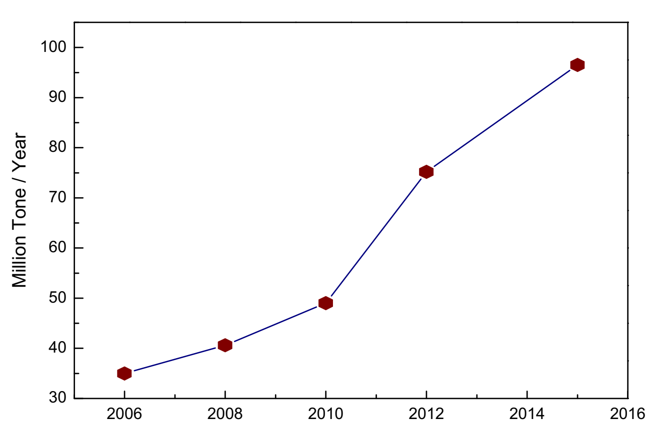


Fig. 2. Global methanol production from 2006 to 2015.

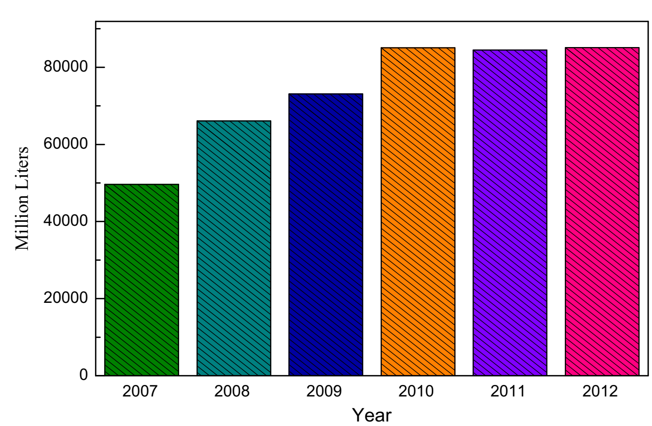


Fig. 3. Global ethanol production.
Source: F.O. Lichts.

sugars (sugar cane, sugar beet, molasses), starches (corn, wheat), or cellulosic biomass (corn stover, straw, grass, wood). The most common feedstock is sugar cane or sugar beet, and the second most common feedstock is corn starch [56]. The use of lignocellulosic biomass is very limited as it requires expensive pretreatment for converting the crystalline structure of cellulose to parent sugars. Although ethanol is produced from sugar beets and molasses, the use of gasohol as an alternative motor fuel has been steadily increasing worldwide for a number of reasons [57,58]. Bioethanol can be derived from a wide range of carbohydrates of general formula $(CH_2O)_n$. Sucrose is fermented using commercial yeast (Saccharomyces *cerevisiae*). The chemical reaction comprises the enzymatic hydrolysis of sucrose followed by the fermentation of simple sugars [59–61]. Invertase enzyme in the yeast catalyzes the hydrolysis of sucrose to convert it into glucose and fructose and then zymase, another yeast enzyme, converts the glucose and the fructose into ethanol. A major processing step in ethanol plants is enzymatic saccharification of cellulose to sugars, which requires lengthy processing and normally follows a short-term pre-treatment step [62].

Bioethanol is used in beverages as well as in the manufacture of pharmaceuticals and cosmetics. In fact, ethanol is the oldest synthetic organic chemical used by humans. The global production of first-generation bioethanol was about 51 billion liters in 2006, comprising 35% of all fuels produced. Fig. 3 shows worldwide ethanol production by the end of 2012.

From Fig. 3, it is evident that worldwide ethanol production increased two-fold, from 39,252 million liters in 2007 to 85,088 million liters in 2012 and is expected to grow fivefold by the end of 2025 [63]. Bioethanol currently accounts for more than 94% of global biofuel production. About 60% of global bioethanol production comes from sugarcane and 40% from other crops. The United States (54,580 million liters as of 2012) and South America (21,335 million liters as of 2012) are the world leaders, together accounting for about 89% of the world bioethanol production using sugarcane and corn, respectively. The USA production as of 2012 amounts to the world production in 2007 (49,625 million liters) [63]. The increasing production and use of ethanol as a fuel can decrease dependency on foreign oil, decrease trade deficits, create employment opportunities in rural regions, minimize air pollution, and address the global warming problem.

3.3. Butanol

Increasing interest in butanol as a sustainable automobile fuel since the late 1990 s has led to a search for enhanced biobutanol production processes that are more cost effective than petrochemical production processes [64]. Even though commercial butanol is currently produced exclusively by petrochemical routes, its production via microbial fermentation is not a new concept. Acetone–butanol–ethanol (ABE) fermentation is promoted by bacteria of the genus Clostridium species, particularly acetobutylicum, as it secretes numerous enzymes that facilitate the breakdown of polymeric carbohydrates in to monomers [65–68]. This is in fact one of the oldest known anaerobic industrial fermentation processes. It is ranked second after ethanol fermentation by the yeast *Saccharomyces cerevisiae* in scale of production, and is one of the largest biotechnological processes ever known [69]. This fermentation technique was the only biotechnological method used on an industrial scale until the first half of the twentieth century, producing 66% of the butanol consumed globally [70]. However, due to the beginning of Second World War and growth of the petrochemical industry, its production quickly declined. By the 1960 s, this fermentation technique was completely replaced by oil refining processes because of the increasing costs of biomass feedstock and low sugar content in molasses (the leading feedstock at the time).

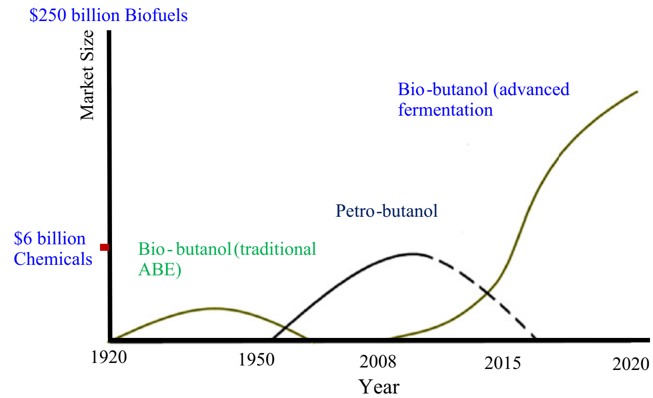


Fig. 4. Schematic of the butanol market.
Source: Green Biologics.

Due to the oil crisis coupled with the uncertainty of petroleum supplies in increasingly energy-driven societies worldwide and emergent environmental awareness, surging oil prices at the beginning of the 1970s led to increased interest in revival of this bio-industry [70,71]. Since then, substantial research and development efforts have focused on various aspects of the ABE process. Biotechnological and molecular biological researches have made major innovations in strain/mutant improvement that dramatically enhance microbial tolerance of butanol toxicity, which led to major increases in ABE solvent production yield [72].

In 1996, the annual worldwide production of butanol was 2.49×10^9 kg. It is estimated that around 10–15 billion lbs of butanol is currently produced annually [73]. The worldwide market for *n*-butanol is about three million tons per year and is predicted to grow at a rate of 3.2% per year through 2025. The current global market value of all biofuels is around $50 billion and is growing at a rate of 7.5% per year. This market is expected to grow to around $250 billion [74] and biobutanol is expected to become a leading biofuel as shown in Fig. 4.

Current fuel demand is met by ethanol and biodiesel, but there is a need for advanced fuels with superior technical properties and first-class sustainability credentials. Due to its superior properties, biobutanol remains the most attractive advanced biofuel and its production is expected to become one of the most widespread fermentation processes, along with that of ethanol over the next 10–15 years [74].

China has made considerable efforts in re-commercializing the ABE fermentation process. Recently, more than $200 million was invested by the Chinese government to build plants with a total of 0.21 million ton per annum (TPA) of solvent capacity and plans to increase to 1 million TPA. There are currently six major plants in China which produce approximately 30,000 t of butanol annually from corn starch [75]. Since biobutanol is produced from the same biomass feedstocks as bioethanol (i.e. corn, wheat, sugar beet and sugarcane), it is attractive to farmers worldwide, who would gain another marketing opportunity for key agricultural residual products.

Biobutanol is an exceptional renewable liquid transportation biofuel because of its superior properties [76]. It is by chance that new and advanced processes for handling and consuming crude glycerol (a co-product) obtained from biodiesel production processes have been developed, which convert, for example, crude glycerol into high value-added products such as butanol, and 1,3-propandiol and ethanol in significant amount via anaerobic fermentation [77]. This is fortunate since the growing demand for biodiesel production causes severe complications with the disposal of by-product crude glycerol (amounting to 10% by

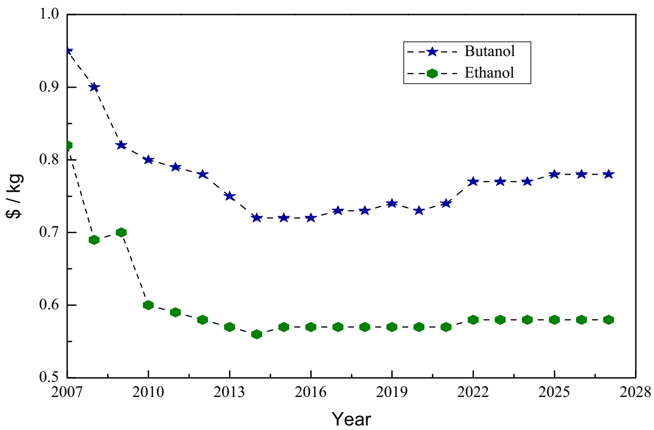


Fig. 5. Projected prices of ethanol and butanol based on expected future market and historical trends [86].

weight) and its conversion to pure glycerol is no longer economically viable due to decreasing prices. The successful production of butanol from glycerol, a byproduct of biodiesel, has been reported by several researchers [78].

3.4. Summary and future research directions

The available evidences suggest that the productions of biomethanol, bioethanol and biobutanol have increased considerably in the last decade. The production of ethanol is greater [63] than those of methanol and butanol. The USA and Brazil are the top producers of ethanol, while butanol is considered the best fuel due to its technical benefits.

The production of biofuels will only remain valuable if biofuels are cultivated in sustainable ways both in terms of biodiversity and the cost benefit of using biomass as food vs. fuel [79]. Continuous use of the food grains for biofuel production could lead to food crunch. Hence, the utilization of inedible biomass (cellulosic) such as the stems, stalks and leaves of the plants may be a viable option. Existing methods for the production of biofuels from cellulosic materials are not economical, but sustainable energy solutions could be identified by applying advanced plant breeding and biotechnology techniques to dedicated energy crops.

An alternative non-dietary biomass and algal biomass containing a considerable amount of carbohydrates and few lignin have been identified as another substrate for butanol production. Further, the growth of autotrophic algae that utilizes environmental CO_2 might contribute to the reduction in global warming. Challenges in enhancing the growth and pretreatment of algal biomass are the center point of present research efforts with a vast scope for further improvements. [80]. The development and use of biofuels as alternatives to fossil fuels still requires more advanced technologies to enhance energy balance and reduce emissions and production costs.

Biobutanol is compatible with existing fuel infrastructures. It has better energy density and performance than ethanol, and can also be produced from more sustainable feedstocks. Therefore, biobutanol has the potential to substitute for both ethanol and methanol, and could make significant contributions towards meeting the demand for next generation biofuels.

4. Economic of methanol, ethanol and butanol production from different feedstocks

The cost of bio-fuels is also an important consideration. Biofuels must be competitive with each other and with mineral fuels such as petrol, diesel and gasoline. The recent market price fluctuations for fuels and feedstocks have been dramatic. In 2008–2009, when petroleum prices peaked at US$ 145/bbl (barrel), the average corn prices ranged from US$ 2 to US$ 4.20 per bushel with spot prices rising over $8 per bushel, and butanol prices soared to nearly US$ 8.50/gal (gallon) compared with its relatively stable price of US$ 4.00/gal [81].

The cost of alcohol production varies according to the cost of the feedstock used and the scale of production. Therefore, the costs of production vary from country to country depending on the type of feedstock used. Thomas et al. [50] estimated that in Europe the production cost of methanol (664 euro/ton) was equivalent to petrol prices.

The largest producer of ethanol is the USA, and approximately 85% of ethanol produced in the USA is based on corn feedstock. The cost of producing ethanol from corn is estimated to be about US$ 1.10/gal. Although there is currently no method for the commercial production of ethanol from cellulosic feedstocks such as agricultural waste, grasses and wood, the estimated production cost of using these feedstocks is US$ 1.15 to US$ 1.43/gal [82]. Because one gallon of ethanol yields less energy than one gallon of gasoline, the production cost of ethanol must be multiplied by a factor of 1.5 to make energy–cost comparisons [83]. This means that if ethanol costs US$1.10/gal to produce, then the effective cost per gallon to equal the energy contained in a gallon of gasoline is US$1.65. In contrast, the current wholesale price of gasoline is about 90 cents/gal [83].

The federal motor fuel excise tax on gasohol, a blended fuel of 10% ethanol and 90% gasoline, is 5.4 cents less per gallon than the tax on straight gasoline. In other words, the federal subsidy is 54 cents/gal for ethanol when the ethanol is blended with gasoline. This subsidy makes ethanol-blended fuel competitive in the marketplace and stimulates the growth of ethanol production and distribution infrastructure.

A detailed comparative analysis of the production economics of current and future biofuels, including ethanol and butanol was performed by Tao et al. [84]. They estimated the corn to ethanol production cost to be US$1.53/gal (0.40/L) and from corn to butanol to be US$1.96/gal (0.52/L) while the production cost of ethanol from sugar cane (in Brazil) was US$1.29/gal (0.34/L). On the other hand, the production cost for petroleum diesel fuel was reported as US$ 0.76/gal [85], but after processing and taxes the prices of petroleum are higher than those of biofuels. Utilizing US Department of Energy historical data and assumptions about prices, demand and supply trends, as well as industry information, Pfromm et al. [86] produced estimated projections for the prices of ethanol and butanol over 20 years, from 2007 to 2027 (Fig. 5).

Based on the technical and economic assumptions used in this study [86], the production of *n*-butanol is not attractive when compared with traditional yeast-based ethanol production from corn. Pfromm et al. reported that average ethanol prices over the 20-year period from 2007 to 2027 would be about US$0.59 per kg with a standard deviation of about US$0.07 per kg, compared to *n*-butanol at US$0.77/kg ± US$0.06/kg. Further, Edward [87] compared the prices of synthetic butanol and oil prices in China during 2010 and found that the prices of butanol were lower than those of oil.

Several recent economic studies of the production of butanol using various substrate sources and processing schemes have been conducted [88]. In these studies it was found that the recovery of butanol by distillation of fermentation broth was not cost effective when compared to petro-chemically-derived butanol. However, the development and optimization of microbial cultures (metabolic/genetic engineering and media formulation), processing technologies, and use of waste substrates may make butanol recovery more economical in coming years.

By the end of July 2011 the average prices of gasoline, diesel, ethanol and butanol in the USA were US$ 3.641/gal, 3.899/gallon,1.8392/gal and 4.0/gal, respectively [89]. The advanced biotechnological production of biofuels from non-edible feed stocks is expected to decrease biofuel production costs.

4.1. Summary

Based on the fact that the production of biofuels (alcohols) is cost effective, in addition to the speedily diminishing petroleum resources and advanced technological innovations, it can be predicted that bioethanol, biobutanol and their blends with petroleum fuels will be viable diesel engine fuels in the near future.

5. Effects of diesel–alcohol blends on performance and emissions of diesel engines

The diesel engine is the most proficient power system among all known types of internal combustion engines. Heavy automobiles, urban motor vehicles, and engineering equipment are driven by diesel engines all over the globe. Diesel automobiles are becoming more popular, and diesel engines are likely to become dominant power systems in future vehicles. Before that occurs, however, further advancement of diesel emissions controls is required as stricter global environmental protocols call for cutting-edge emission controls and near-zero diesel emission levels in the years to come [1].

In order to achieve diesel engine emission reduction many techniques have been employed. The blending of oxygenates such as alcohols with diesel fuel to provide more oxygen during combustion has been reported as one of the promising methods for controlling diesel engine emissions. There are numerous methods of alcohol diesel dual fuel operation. The ignition of alcohol in dual fuel operation is ensured by the high self-ignition of diesel fuel. The most common methods for achieving dual fuel operation are (I) alcohol–diesel fuel blends, (II) alcohol–diesel fuel emulsions, (III) dual injection, and (IV) alcohol fumigation. The simplest way to use alcohol in diesel engine is in the form of blends. Numerous studies have been executed on CI engines to observe the engine performance and exhaust emissions using alcohol–diesel blends [90–95]. Collectively these studies indicate that alcohol blends can improve some exhaust emissions without having any adverse effect on performance of diesel engine. The effects of different diesel–alcohol blends on the combustion, performance and emissions of diesel engines are discussed below.

5.1. Methanol–diesel fuel blends

The use of methanol for diesel engines has been investigated in several studies [14] because of its advantages over traditional fuels. Methanol behaves much like petroleum, so it can be stored and transported in the same manner. It has better lean combustion characteristics than hydrocarbon fuels. Methanol has been used as a large volume motor fuel substitute during gasoline shortages. It was frequently used in the early twentieth century to fuel automobiles before economical gasoline was extensively introduced. Chemically synthesized methanol was used as a diesel engine fuel in Germany during World War II. The use of methanol as an automobile fuel received attention during the oil crisis of the 1970s due to its accessibility and low cost.

The use of methanol either as a blend with conventional fuels or as an additive in biodiesel production, has received growing attention. Because of its higher octane number and oxygen content, the utilization of methanol in compression ignition engines yields better results than gasoline [96]. Methanol has many advantages as a diesel engine fuel, including lower ozone forming potential, negligible NO_x emissions, lack of sulfur and sulfur compounds, and easy refueling. However, there are difficulties in the ignition of air–fuel mixtures when methanol is used in diesel engines, mainly due to its low CN, high latent heat of vaporization and long ignition delay [97]. Another factor that affects the driveability of automobiles fueled with methanol–diesel blends is the solubility of methanol in neat diesel fuel. Methanol and diesel fuel are not completely miscible. Moreover, the presence of a very small amount of water can cause methanol–diesel mixture to separate in to diesel and water-methanol phases [98]. Because of the miscibility problem, phase separation, and low CN, the ratio of methanol to diesel has to be low to avoid adverse effects on combustion, even for relatively small additions of methanol. In order to overcome these problems and facilitate the use of methanol in diesel engines, methods such as alcohol fumigation, dual injection, and methanol–diesel fuel emulsion [99] have been employed [100,101].

An investigation regarding the formulation of stable mixtures of diesel fuels with methanol was reported by Azev et al. [102]. They studied the influence of the hydrocarbon composition of the fuel, and additions of water, higher alcohols, surfactants and aromatic hydrocarbon on the solubility of methanol in diesel fuel. Aromatic hydrocarbons in diesel fuel were found to have almost no effect on the solubility of methanol. However, the addition of 10% water to methanol resulted in an emulsion (methanol content 5%) that remained for several days, forming suspended drops of methanol in diesel fuel. When the most effective surfactants were used they formed a comparatively stable water-fuel emulsion (no layer separation up to 15 days), containing 5% methanol, 0.5% water, and 0.25% surfactant (sodium salt of the dibutyl-ester of sulfosuccinic acid). The stability of this four-component system decreased with increasing water content. It was also found that higher alcohols, particularly butanol, can be utilized to stabilize methanol–diesel fuel blends.

Since using methanol blended with diesel fuel may reduce air pollution, many studies have addressed the effects of this alternative fuel on the performance, combustion and exhaust emissions of diesel engines. Huang et al. [103] used various blend ratios of methanol–diesel fuels in engine tests and found that the smoke, CO and THC emissions decreased, but NO_x emissions increased with increasing methanol content.

Najafi and Yusaf [104] examined the consequences of using methanol–diesel fuel blends in diesel engine at mixing ratios of 10:90, 20:80 and 30:70. The output power and torque of neat diesel fuel was found to be lower than those of methanol–diesel blends. The mixing ratio that produced the lowest exhaust temperature was 10% methanol in 90% diesel fuel. The exhaust temperature for diesel fuel was higher than that of blended fuel. The brake specific fuel consumption (BSFC) did not vary significantly, but the lowest was associated with the 30% methanol blend. However, the methanol–diesel fuel blends resulted in improved brake thermal efficiency (BTE) compared to diesel fuel under almost all operating conditions.

Huang et al. [105] studied the combustion behavior of a CI engine fueled with diesel–methanol blends under various fuel delivery advance angles. The heat release rate in the premixed burning phase increased and the combustion duration of the diffusive burning phase both decreased as the methanol mass fraction in the diesel–methanol blends increased. The ignition delay, rapid burn duration and total combustion duration increased as the fuel delivery advance angle increased for both diesel fuel and diesel–methanol blends. The center of the heat release curve approached the top-dead-center, and the maximum cylinder gas pressure, the maximum rate of pressure rise, and the

heat release rate all increased as the fuel delivery advance angle of the diesel–methanol blends increased.

Further, Huang et al. [106] prepared oxygenated fuel blends by adding methanol and a solvent to diesel fuel, and evaluated the performance and emissions of oxygenated blends in a CI engine under various fuel delivery advance angles. The thermal efficiency of the engine increased and BSFC decreased with increases in the fuel delivery advance angle. The NO_x concentration in the oxygenated blends increased as the fuel delivery advance angle increased, while the NO_x concentration decreased with the addition of large amounts of oxygenates to diesel fuel blends for specific fuel delivery advance angles. The blending of oxygenates with diesel fuel had stronger impacts on the NO_x concentrations at high engine loads than at low engine loads. The CO content decreased as the fuel delivery advance angle at high engine loads decreased, whereas at intermediate and low loads, the CO content varied only slightly with variation of the fuel delivery advance angle but was generally low for diesel–oxygenate blends. The fuel delivery advance angle had slight effects on the HC content of the diesel–oxygenate blends. The quantity of smoke was reduced as the fuel delivery advance angles for both diesel fuel and diesel–oxygenate blends were increased.

Chao et al. [107] studied the effects of methanol containing additive on the emissions characteristics of a heavy-duty diesel engine, and found that the addition of a moderate amount of methanol containing additive reduced air pollutants, including NO_x, PM and polynuclear aromatic hydrocarbons (PAHs) emitted by a diesel engine.

Sayin et al. [108] assessed the performance and exhaust emissions of a direct injection (DI) diesel engine, using methanol–diesel (M5, M10) and ethanol–diesel (E5, E10) blends. The engine torque was fixed at 30Nm while the engine speed varied between 1000 and 1800 rpm. Dodecanol was added to stabilize the blends. The use of fuel blends caused decreases in the emissions of smoke, CO and THC. However, NO_x emissions were increased when blends were used. The BSFC was also increased for both blends mainly due to the lower heating value (LHV) of methanol and ethanol. The increase in BSFC associated with the M10 blend was higher than that of E10, and the BSFC value with the M5 blend was higher than that of E5. All fuel blends produced a decrease in BTE, and the lowest BTE was obtained with M10.

A similar study of the performance and combustion characteristics of a single cylinder, 4-stroke DI diesel engine fueled with biodiesel-diesel–methanol blend fuel was performed by Qi et al. [109]. They found that, when M5, and M10 (methanol 5% and 10%) were added to BD 50 (50% biodiesel and 50% diesel), combustion started later for BDM5 (biodiesel/diesel/methanol) and BDM10 than for BD50 at low engine loads, but started at almost the same time at a high engine loads. The power and torque outputs of BDM5 and BDM10 were slightly lower than that of BD50. BDM5 and BDM10 dramatically reduced smoke emissions. CO emissions were somewhat lower, and NO_x and HC emissions were almost comparable to those of BD50 at full engine load.

Recently, Zhang et al. [110] investigated the combustion characteristics and emissions of a 4100 turbocharged diesel engine fueled with diesel (80%), M10 (methanol10%), and iso-octanol and isooctyl nitrate (10%) or MDE (dimethyl ether 10%). They found that the maximum cylinder pressure and peak heat release rate during the initial stage of combustion for M10 with isooctanol and isooctyl nitrate were higher than those of diesel, while NO_x emissions were slightly higher and the soot emissions were lower than those of diesel. However, both the maximum cylinder pressure and peak heat release rate for M10 fuel with dimethyl ether were lower than those of diesel fuel, and the NO_x and soot emissions were decreased. The power of the blended fuel was lower than that of diesel fuel, while the HC emissions were slightly increased and CO emissions were slightly decreased.

Song et al. [111] studied the effects of a dual fuel system on a CI engine operating at three different loads (low load 0.35 MPa, middle load 0.56, and full load 0.77 MPa) and at two different speeds (1600 and 200 rpm). The main objectives of this study were to identify the optimal dual fuel operation conditions and to investigate effects of methanol on dual-fuel engine performance, emission and combustion characteristics. Dual-fuel operation produced equivalent or greater power than a conventional diesel engine with better fuel economy. The BSFC was improved under high-load operating conditions. Smoke emissions were significantly decreased, and a modest reduction in NO_x emissions was observed. However, HC and CO emissions increased when methanol was added.

Yao et al. [112] investigated the effects of diesel–methanol compound combustion (DMCC) in two different four cylinder diesel engines, one naturally aspirated and the other turbocharged. Experiments were performed for both engines at maximum torque speed. The naturally-aspirated engine was tested at 2000 rpm, while the turbocharged engine was tested at 1600 rpm. Diesel fuel was used for starting engines at low load operation. A fixed amount of diesel fuel was maintained while extra energy was supplied via the injection method. In both cases, DMCC was found to decrease BSFC, NO_x, and smoke emissions while CO and HC emissions were increased.

In another study, Yao et al. [94] examined the effects of DMCC and its application to a four cylinder, naturally aspirated DI diesel engine operating at different engine loads (10%, 25%, 50%, 75% and 100%) at 2200 rpm and 3200 rpm, with and without an oxidation catalytic converter. Diesel fuel was used to ignite methanol–air mixture while methanol was injected into the air intake of each cylinder to form a homogeneous mixture when combined with the intake air. Increases in ignition delay, heat release delay, maximum pressure and peak heat release were observed within the DMCC system. The diesel engine operating under the DMCC method exhibited reduced soot and NO_x emissions, while HC and CO emissions were increased compared with those of a neat diesel engine. The DMCC method coupled with an oxidation catalyst has the potential to reduce CO, HC, NO_x and soot emissions.

Popa et al. [113] studied the impacts of methanol–diesel fuel blends on exhaust emissions using two different diesel fuels and methanol engine supply methods. The first method was methanol admission through a carburetor combined with classic diesel fuel injection, and the second method used separate fuel injection. Smoke and NO_x levels were considerably reduced for all engine loads as the quantity of methanol in the blend increased.

Fuel injection systems also play important roles in reducing emissions to acceptable levels. The most important injection characteristics are injection pressure and timing. Injection pressure significantly affects engine performance and exhaust emissions. Icingur and Altiparmak [114] examined the influence of four different injection pressures (100, 150, 200 and 250 bar) and fuel CNs of 46, 51, 54.5 and 61.5 CN in a diesel engine, and found that increasing the injection pressure decreased smoke opacity and increased NO_x and SO_2 emissions.

Payri et al. [115] reported that delayed fuel injection has only a small effect on smoke opacity and NO_x emissions, but leads to higher CO and THC emissions with significant adverse effects on BSFC. At light engine loads, the combination of retarded fuel injection and exhaust gas recirculation (EGR) were very efficient for achieving reduced smoke opacity and NO_x levels.

Sayan et al. [116] reported the effects of injection pressure and timing on the performance and emission characteristics of a single cylinder, four stroke DI diesel engine using methanol

(5%, 10% and 15%) blended-diesel fuel at three different injection pressures (180, 200 and 220 bar) and timings (15°, 20°, and 25° CA (crank angle) before top dead center (BTDC)) at 20 Nm engine load and 2200 rpm. BSFC, break specific energy consumption (BSEC), and NO_x emissions were increased and BTE, smoke opacity, CO and HC were decreased when the volume of methanol in the blend was increased. BSFC, BSEC and NO_x emissions were increased, and BTE, smoke opacity, CO and THC emissions were decreased when the injection timing and pressure were increased or decreased, respectively.

Canakci et al. [117] studied the effects of injection pressure (180, 200, and 220 bar) on the combustion, performance and emission characteristics of a single cylinder, four-stroke, naturally aspirated DI engine. All tests were conducted at four different loads (5, 10, 15, and 20 Nm) at a constant engine speed of 2,200 rpm. The results were similar to their previous study [116]. Increasing injection pressure resulted in increased NO_x and CO_2 emissions while the smoke number, CO, and HC emissions decreased. The best results were attained for HC and CO emissions at a load of 20 Nm and at 5 Nm load for smoke number. On the other hand, decreasing the injection pressure to a 5 Nm load yielded minimum NO_x and CO_2 emissions. The best results for BSFC, BSEC, and BTE were obtained at the original (ORG) injection pressure.

Injection timing also significantly affects engine performance and exhaust emissions. Sayin and Canakci [118] studied the effects of injection timing on the exhaust emissions and performance of a naturally aspirated, single cylinder, four-stroke DI diesel engine using methanol and ethanol-blended diesel fuels at five different injection timings: 21°, 24°, 27°, 30° and 33° (CA BTDC). BSFC, NO_x and CO_2 emissions were increased, and BTE, CO and THC emissions were dramatically decreased as the amount of ethanol in the blend increased. In terms of injection timing, the test results demonstrated that, as injection timing increased, CO and unburned hydrocarbon (UHC) emissions decreased while NO_x and CO_2 emissions increased. Advancing the injection timing 6° CA BTDC (33° CA BTDC) at a 30 Nm load and 1800 rpm yielded the best results in terms of HC and CO emissions. On the other hand, retarding the injection timing 6° CA BTDC (21° CA BTDC) at a 15 Nm load and 1800 rpm resulted in the minimum NO_x and CO_2 emissions. The ORG injection timing yielded the best results with regard to BSFC and BTE.

Canakci et al. [119] calculated the effects of injection timing on the performance, exhaust emissions and combustion characteristics of a single cylinder diesel engine fueled with a methanol (0–15%)—diesel fuel blend at three different injection timings (15°, 20°, and 25 °CA BTDC) and four different loads (5, 10, 15, and 20 Nm) with a constant engine speed of 2200 rpm. BSFC, BSEC, combustion efficiency, NO_x and CO_2 emissions increased as the amount of methanol in the blend increased, while BTE, smoke number and CO emissions decreased. However, as the injection timing was advanced, the smoke number, CO and unburned HC emissions decreased, and NO_x and CO_2 emissions increased. On the other hand, retarding the injection timing at a load of 5 Nm yielded the minimum heat release, combustion efficiency, and NO_x and CO_2 emissions. The ORG injection timing was found to provide the best results for BSFC, BSEC, and BTE.

Sayin et al. [120] studied the performance and exhaust emissions of a single cylinder, DI diesel engine using methanol-blended diesel fuel with methanol content ranging from 0% to 15% in increments of 5% for three different injection timings (15°, 20° and 25 °CA BTDC) and four engine loads (5 Nm, 10 Nm, 15 Nm, 20 Nm) at 2,200 rpm (revolutions per minute). The results revealed that the injection timing and methanol amount play a significant role in the combustion process. The combustion, emissions and engine performance with respect to increasing amounts of methanol, were similar to those observed in a previous study [116]. As the injection timing advanced, the smoke opacity, CO and HC emissions decreased while the NO_x and CO_2 emissions were increased. Advancing the injection timing at a 20 Nm load yielded the best results in terms of HC and CO emissions. On the other hand, retarding the injection timing, a10 Nm load resulted in minimum NO_x and CO_2 emissions. Increasing the methanol ratio in the fuel blend led to an increase in the BSFC and decrease in BTE. The ORG ignition timing led to the best results for BSFC and BTE.

In addition to methanol–diesel blends, the impacts of methanol fumigation on engine performance and emissions have been investigated [121–125]. These studies reported that when methanol fumigation was applied to the diesel engine, the BTE was reduced at low engine load while there were no significant changes at intermediate to high loads. The BSFC was increased. Methanol fumigation had the potential to reduce smoke, NO_x and PM emissions in the whole range of engine operation, but led to significant increases in CO, HC, NO_2, unburned methanol, and formaldehyde emissions. Further, the application of methanol fumigation together with a diesel oxygen catalyst (DOC) has the potential to reduce HC, CO, NO_x and PM emissions simultaneously at intermediate to high engine loads. Therefore, blending and fumigation techniques have similar impacts on emissions and engine performance; however, fumigation has some additional advantages over blending, especially when DOC was applied. The summary of the reported studied is documented in Table 3.

5.1.1. *Summary and future research directions*

The studies described in this paper show that increasing the amount of methanol in methanol–diesel blend significantly decreases smoke, CO, THC and BTE and increases BSFC and NO_x emissions. However, especially in the case of methanol fumigation, NO_x emissions were found to significantly decrease in some studies. Increases in methanol fuel consumption are mainly caused by its low heating value; however, the use of such fuels in turbocharged or low heat release engines improves methanol–diesel fuel engine economy. Engine operating conditions, such as load, speed, injection timing, and injection pressure also influence engine economy and performance. Increasing injection timing and pressure decreases smoke opacity, CO and THC emissions, with a slight penalty on NO_x emissions. Hence, further studies of these conditions should be performed to improve engines and control systems in order to obtain optimal matches.

Additives used to improve blend properties may further increase the combustion performance of engines, and in turn promote fuel economy, and engine power. Therefore, new fuel injection techniques and additives to stabilize diesel–methanol blends should be identified to further enhance engine performance and reduce diesel engine emissions.

5.2. *Ethanol–diesel fuel blends (E-diesel)*

The use of diesel–ethanol blends has been a subject of research since the first investigations were carried out in South Africa in the late 1970s [126]. E-diesel can, in principle, serve as an alternative energy source by displacing diesel, a fossil fuel. Numerous ethanol surrogate technologies are applicable in CI engines such as ethanol blends, ethanol emulsions, ignition supporting additives, dual fuel injection, and fumigation [127].

To date, many investigations have been carried out related to engine performance and emissions with ethanol–diesel blends [127–135]. Hansen et al. and Corkwell et al. [127,128] reviewed the emissions and performance of a CI engine operating on E-diesel fuel blends. They reported that E-diesel has favorable

Table 3
Summary of methanol–diesel blend studies dealing with performance and emissions of diesel engine.

Reference	Engine type	Methanol (%)	Stability additive (%)	Reference fuel	Emissions	Performance	Others parameters
Yao et. al. [94]	4-cylinder naturally aspirated DI diesel engine	n/a	No	Diesel	▼:Soot, NO_x ▲:CO, HC ▼:CO[a], HC[a], soot[a], NO_x[a]	▲:Ignition delay, heat release delay, P_{max}	DMCC, engine loads and speed, DOC
Jikar et al. [96]	F4L 913 4-stroke diesel engine	10 20 30	No	Diesel	n/a	▼:BSFC ▲:BTE Torque	–
Huang et al. [103]	CI engine	n/a	No	Diesel	▲:NO_x, ▼:Smoke, CO, THC	▼:BSFC	Fuel delivery angle
Najafi and Yusuf [104]	F4L 913 4-stroke diesel engine	10 20 30	No	Diesel	n/a	▼:BSFC ▲:BTE, Torque	Mixing ratios
Huang et al. [105]	CI engine	8.96 13.3 17.7	0.92–16.6	Diesel	n/a	▲:P_{max}, Heat release rate	Fuel delivery angle
Huang et al. [106]	CI engine	8.96 13.3 17.7	0.92–16.6	Diesel	▲:NO_x, ▼:NO_x[b] ▼:Smoke, CO —:HC	▼:BSFC ▲:BTE	Fuel delivery angle, engine load
Chao et al. [107]	Heavy-duty diesel engine	5 8 10 15	0–15	Diesel	▲:CO, THC ▼:NO_x, PM, PAHs —:CO_2	n/a	Load, transient cycle
Sayin et al. [108]	Single cylinder 4- stroke naturally aspirated DI (Super Star 7710) diesel engine	5 10	1	Euro-diesel	▲: NO_x ▼:Smoke opacity, CO, THC	▲:BSFC ▼:BTE	Engine speed, engine torque
Qi et al. [109]	Single cylinder 4-stroke DI engine	5 10	4	50% Biodiesel and 50% Diesel	▼:Smoke, CO —:NO_x, HC	▼:Power and torque output	Engine load
Zhang et al. [110]	Turbocharged diesel engine	10	10	Diesel	▲:NO_x, HC ▼:Soot, CO ▼:NO_x[c]	▲:P_{max}, Heat release rate	Stability additive
Song et al. [111]	Single-cylinder 4-stroke water-cooled DI engine	10–80	No	Diesel	▲:CO, HC ▼:NO_x, Smoke	▲:BSFC	Injection pressure and timing, engine load, speed
Yao et al. [112]	4-cylinder 4-stroke naturally aspirated DI and turbocharged engine	n/a	No	Diesel	▲:CO, HC ▼:NO_x, Smoke	▼:BSFC	Engine load, DMCC
Popa et al. [113]	D 115 multi-sprays type, D 2156 MTN 8 type turbocharged engine	50	No	Diesel	▼:Smoke, NO_x	▲:BSFC	Engine loads and speed
Sayan et al. [116]	Single cylinder, 4-stroke DI diesel engine	5 10 15	No	Diesel	▲:NO_x ▼:Smoke, CO, THC	▲:BSFC, BSEC ▼:BTE	Injection timing and pressure
Canakci et al. [117]	Single cylinder, 4- stroke naturally aspirated DI diesel engine	5 10 15	No	Diesel	▲:NO_x, CO_2 ▼:CO, Smoke, UHC	▲:BSFC, BSEC, Combustion efficiency ▼:BTE, Heat release rate, P_{max}	Injection pressure
Sayin et al. [118]	Single cylinder, 4-stroke naturally aspirated DI diesel engine	5 10 15	No	Diesel	▲:NO_x, CO_2 ▼:CO, THC	▲:BSFC ▼:BTE	Injection timing
Canakci et al. [119]	Single-cylinder, 4-stroke DI naturally aspirated CI engine	5 10 15	No	Diesel	▲:NO_x, CO_2 ▼:CO, Smoke, UHC, P_{max}, Heat release	▲:BSFC, BSEC, Combustion efficiency ▼:BTE	Injection timing
Sayin. [120]	Single cylinder 4-stroke naturally aspirated DI diesel engine	5 10 15	No	Diesel	▲:NO_x, CO_2 ▼:CO, Smoke, UHC	▲:BSFC ▼:BTE	Injection timing

Cheung et al. [121]	4-cylinder, naturally aspirated DI diesel engine	10 20 30	No	Euro V diesel	▲:CO, HC, NO_2, HCHO ▼:NO_x, PM ▼:CO^a, HC^a, $NO_2{}^a$, $HCHO^a$	▼:BTE	Port injection, engine load, DOC
Udyakumar et al. [122]	Single cylinder 4-stroke DI diesel engine	25 50 75	No	Diesel	▼:Smoke, NO_x	▲:SEC ▼:BTE	Fumigation
Cheng et al. [123]	4-cylinder DI diesel engine	10 20 30	No	Diesel	▲:HC, CO, NO_2 ▼:Smoke, PM	▼:BTE	Fumigation
Zhang et al. [124]	4-cylinder, naturally aspirated DI diesel engine	10 20 30	No	Euro V diesel	▲:HC, CO, NO_2 ▼:CO_2,NO_x, Smoke, PM ▼:HC^a, CO^a, $NO_2{}^a$, PM^a	▼:BTE	Fumigation, DOC
Zhang et. al. [125]	4-cylinder naturally aspirated DI diesel engine	10 20	No	Euro V diesel	▲:HC, CO, NO_2 ▼:NO_x, PM	▲:BSFC ▼:BTE ▲:BTE^b	Fumigation

▲, Increase; ▼, Decrease; —, no change; n/a, not available.
[a] effect of diesel oxidation catalyst.
[b] at high load.
[c] effect of dimethyl ether.

effects on engine performance and emissions. In this section we provide a comprehensive review of the latest research regarding combustion behavior as well as the performance and emissions of engines using E-diesel. The effects of adding ethanol at 10%, 25% and 50% concentrations to diesel fuel on the performance and emissions of direct-injection and pre-chamber diesel engines were investigated using three different ethanol introduction methods (fumigation, inline mixing, stabilized emulsions), and diesel–ethanol blends, 10E, 15E and 20E (ethanol 10%, 15% and 20%) using a commercial DII-3 CN improver. The thermal efficiency was similar to that of neat diesel fuel, while CO and HC emissions were higher at light load and at heavy loads HC and CO were reduced with a small increase in NO_x emissions [129] that could be reduced by adjusting the injection timing [130]. Meanwhile, a significant reduction in NO_x with increases in CO and HC emissions and thermal efficiency were reported for a fumigated four-cylinder turbocharged diesel engine using ethanol and water mixtures [131]. Significant reductions in PM and NO emissions in comparison with pure diesel fuel have also been observed [132–133].

Koganti et al. [134] studied the effect of a 5% ethanol diesel fuel blend in a three cylinder, four-stroke DI tractor engine. CO and PM emissions were reduced, but NO_x emissions were increased. Further, slight drops in engine power and torque were noted with a corresponding loss of fuel economy.

Ethanol–diesel blends (E5, E10, E15 and E20), were reported to increase the BSFC up to 9% for a 20% ethanol blend compared to diesel fuel alone in a stationary diesel engine operated at a constant speed. The use of these blends also reduced the exhaust gas temperature and lubricating oil temperature, without any significant power reduction while CO and NO_x emissions were reduced up to 62% and 24%, respectively [135].

In another investigation, a diesel engine operated at constant speed was fueled with neat diesel fuel, and 2%, 4% and 6% ethanol–diesel blends at compression ratios of 19, 21 and 23, respectively. The addition of 4% ethanol to diesel fuel increased the power output and efficiency of the engine while BSFC was decreased over a range of compression ratios. The best efficiency was attained at a compression ratio of 21 with an increment ratio over 3.5% [136].

Further, Li et al. [137] studied the effects of 5%, 10%, 15% and 20% ethanol–diesel blends in a single-cylinder DI diesel engine and found that BTE, BSFC, and THC were increased while CO, NO_x and smoke were significantly reduced in comparison with neat diesel fuel.

Rakopoulos et al. [138] studied the effects of ethanol blends (5% and 10% by volume) compared with conventional diesel fuel, on the performance and emissions of a turbocharged, DI diesel engine. CO and NO_x emissions decreased, while THC emissions increased with the use of ethanol. BSFC increased and BTE decreased as the amount of ethanol increased.

Arapatsakos [139] used diesel–ethanol blends in a tractor engine under full load and studied their effects on exhaust emissions. The addition of ethanol had favorable effects on CO and HC emissions but a negative effect on engine power due to the small calorific value of ethanol.

Rakopoulos et al. [140] conducted an experimental study to evaluate and compare the use of ethanol as a supplement to conventional diesel fuel at different blend ratios (E5, E10, E15) in a high speed, DI diesel engine working at a speed of 2,000 rpm under four different loads. Smoke density and CO were significantly reduced, while NO_x emissions were only slightly decreased with the use of ethanol–diesel fuel blends compared to the neat diesel fuel. A further reduction in NO_x emissions was achieved by increasing the percentage of ethanol in the blend. On the other hand, HC emissions increased with the use of the ethanol–diesel

fuel blends. However, as the percentage of ethanol in the blends increased, slight increases in specific fuel consumption and BTE were observed.

Song et al. [141] investigated carbonyl emissions from a heavy-duty DI diesel engine fueled with pure diesel fuel and ethanol–diesel fuels blends at 1,200, 1,800 and 2,600 rpm. The experimental results revealed that acetaldehyde was the foremost carbonyl produced by both fuels, followed by formaldehyde, acrolein, acetone, propionaldehyde and crotonaldehyde. The addition of ethanol to diesel fuel resulted in a decrease in acrolein emissions, while the other carbonyls increased at low engine speed. The brake specific emissions of each carbonyl compound decreased with increasing engine load during the constant speed test. Carbonyl carbon (CBC) emissions from both pure diesel and diesel–ethanol blends were highest at high engine speed, while total CBC emissions from ethanol–diesel fuel were higher than those from diesel fuel under most engine operating conditions.

Atmospheric pressures were taken into account in order to study the effects of ethanol–diesel blends (10%, 15%, 20% and 30%) on performance and emissions in a turbo-charged diesel engine under different atmospheric pressures (81, 90 and 100 kPa) and to compare them with those of neat diesel fuel. BSFC was significantly improved below 90 kPa, but sharp increases in HC and CO emissions with increasing engine speed, load and ethanol concentration were observed at 81 kPa. On the other hand, atmospheric pressure and ethanol blending percentage did not affect NO_x emissions at 90 and 100 kPa, while smoke was reduced below 90 kPa [142].

The most important advantage of E-diesel is that it can be used in diesel engines without any modification to the engine. Hence, a considerable amount of research has focused on diesel–ethanol blends, but drawbacks to the addition of ethanol to diesel fuel remain. One of the primary problems is that ethanol has a low CN, and therefore the addition of ethanol may decrease the CN of the diesel fuel. Modern diesel engines require fuels with CNs of 40 or higher to maximize performance and minimize emissions. Ethanol has a CN of approximately 8. This problem can be solved by adding cetane-enhancing additives such as 2-ethylhexylnitrate.

The use of ethanol with additives such as CN improver can sharply reduce particulate emissions. The extent of improvement differs from engine to engine and also according to the operational range of the engine. However, the viscosity and lubricity of blends decline, and CN decreases linearly at ambient temperatures. Hence, ignition enhancers and other additives are mandatory to enhance the ignition and life span of diesel engines when ethanol–diesel fuel blends are used. The power of ethanol to decrease particulate emissions increases flexibility in the control of NO_x emissions under diverse engine working environments. Additional ecological benefits related to the use of ethanol–diesel fuel blends include enhanced biodegradability and declines in greenhouse gas emissions if ethanol is synthesized from biomass resources.

Other problems associated with the use of ethanol blended with diesel fuel are its low viscosity and lubricating power, which can degrade the lubricity of diesel fuel. The diesel fuel injection method requires that the fuel can lubricate closely fitting parts of the engine. In addition, ethanol has a low flash point. In general, diesel fuel has a flash point of about 52–65 °C, which means that accidental ignition is rare. However, in the presence of ethanol, the flashpoint will be below ambient temperature, and therefore E-diesel needs to be handled with more caution than neat diesel.

Due to the low miscibility of ethanol with diesel fuel, ethanol does not blend efficiently with diesel to form consistent solutions, which results in phase separation. The miscibility of ethanol in diesel relies on hydrocarbon amount and wax content of the base diesel, ethanol content (low ethanol concentration has reduced immiscibility), and the temperature of the diesel fuel [135]. The reduction of diesel aromatic content decreases the miscibility of ethanol. The main advantage of ethanol–diesel blends is its consistency at low temperatures (up to 10–11 °C). Anhydrous ethanol has good blending power to mix with diesel fuel and forms consistent solutions of up to 5% ethanol at warm ambient temperatures. However, ethanol has been found to be immiscible in diesel fuel at temperatures below 10 °C, at which point the blend splits into two separate phases. This affects the fluidity and filterability of E-diesel in cold conditions [128].

Solubility also relies on the amount of water present in ethanol. Being hygroscopic, ethanol easily absorbs water from ambient air and supply systems. Anhydrous ethanol is readily miscible with diesel fuel at ratios of 0–30% and 70–100%. Within these zones, mixture miscibility and cloudiness followed by phase separation are observed when the water content of the ethanol surpassed 1% [14]. Therefore, low temperatures and water contamination decreases the E-diesel stability mainly due to phase separation. For stabilizing ethanol–diesel fuel blends especially in the context of large amounts of water, and to ensure fuel homogeneity under all temperature conditions, mixing a suitable amount of appropriate additives into E-diesel is mandatory [14,139]. However, such additives may increase the cost of the fuel.

In order to maintain the stability of E-diesel blends, two types of additive methodologies are normally employed: the addition of surfactants (emulsifiers) that yield stable emulsions or micro emulsions, and the addition of co-solvents that generate consistent blends. Co-solvents behave as connecting agents through molecular compatibility and bonding to form stable blends. The formulation of E-diesel blends with surfactants is more complex, and generally necessitates heating and rousing. A micro-emulsion consists of droplets or micelles of ethanol dispersed in the diesel fuel phase, and a minor quantity of emulsifier and water are necessary for its formulation. E-diesel preparations are usually micro-emulsions. A study from the1980s concentrated on emulsifiers, and the first E-diesel micro-emulsion was designated by Moses et al. [143], in which about 2% of a commercial surfactant was found to be desirable for each 5% of aqueous ethanol (5% water) added to diesel fuel. This combination formed an impulsive, crystal clear, and thermodynamically stable blend.

In 1982 Boruff et al. [144] utilized a blend of two surfactants, N, N-dimethylethanolamine and unsaturated fatty acids, with aqueous ethanol and diesel and observed that the blends were stable at temperatures as low as −15.50 °C. Since then, emulsifier technology has progressed, and today less than 1 vol% is required under certain circumstances.

Four different ethanol-*n*-butanol–diesel micro-emulsions, with fuel properties such as relative density, kinematic viscosity, and gross heat of combustion similar to those of diesel fuel were tested by Bhattacharya et al. [145] in a constant-speed, DI diesel engine. The power-producing capability of the engine using these micro-emulsions was similar to that diesel fuel. The CO emissions were marginally lower, but the HC and NO_x emissions were higher when micro-emulsions were used. Further, the effects of emulsifiers on performance, combustion and emission characteristics with different blends (D80/E13/EA07, D70/E17/EA13, and D60/E23/EA17) in a DI diesel engine were reported by Kumar et al. [146]. They used ethanol–diesel micro-emulsions with ethyl acetate (EA) as an additive/ingredient for blends. Phase separation did not occur in the D80/E13/EA07 blend, for which the BSE and thermal efficiency were improved without any power reduction at a lower load. NO_x and smoke emissions decreased while HC and CO emissions increased at lower loads. HC and CO emissions improved at higher loads, but BSFC increased.

Emulsified ethanol–diesel blends (30%, 40% and 50%) using sorbitan monooleate as a surfactant were investigated in a single

cylinder, four-stroke diesel engine to determine the effects of blend ratios on performance, combustion and emissions. The 50% ethanol–diesel blend was best, compared to pure diesel and other blend ratios. Using the optimal blend, the delay period was reduced at a 24° injection angle. BTE and NO_x emissions increased, but smoke density and PM were reduced, and the maximum heat release, peak pressure, cumulative heat release and cylinder pressure were increased [147].

Recently, a biofuel and castor oil-based emulsifier was developed to keep the diesel–ethanol blend stable and homogenous [93]. This emulsified fuel was found to decrease BSFC, smoke and NO_x emissions while BTE, THC and CO emissions increased. Further, many studies have been carried out to identify suitable additives (co-solvents) to maintain the homogeneity and stability of E-diesel blends and improve engine performance while reducing pollutant emissions [13,14].

Can et al. [148] found that the addition of ethanol at different ratios (10–30 vol%) containing an unsaturated fatty acid-based solvent as an additive and isooctyl nitrate as an ignition improver changed physicochemical properties and enhanced the stability of the blend. In addition, they found that emissions varied with changes in engine operating conditions, ethanol content, additives and ignition improver. Moreover, the additions of multi-component biodiesel, fatty acid methyl and ethyl ester (rapeseed oil methyl and ethyl ester) to E-diesel blends was investigated, and it was found that blends form instantaneously over a wide range of biodiesel and E-diesel concentrations [149].

The influences of ether additives in E-diesel blends on physicochemical properties such as density, volatility, viscosity, characteristics at cold temperatures, CN, and performance in engine tests were assessed by De Menezes et al. and Adam et al. [10,150]. They determined that ethyl tert-butyl ether (ETBE) and tert-amyl ethyl ether (TAEE) act as co-solvents for ethanol–diesel fuel blends. The additions of ethanol and ETBE considerably modify volatility (flash point and distillation curve) and decrease the cetane number, spoiling the fuel's performance in engine tests. The use of ethers in ethanol–diesel formulations makes ethanol compatible with diesel in the presence of a small amount (0.5% v/v) of water in ethanol. ETBE and TAEE ethers are entirely miscible in diesel and ethanol.

Adam et al. [150] reported that ethanol and methyl-tert-butyl ether (MTBE), although helpful in decreasing atmospheric pollution, may increase groundwater pollution due to the co-solvency of petroleum hydrocarbons and by providing better microbial substrates. MTBE reveals the need to comprehensively assess possible positive and negative ecological effects related to fuel choices, referred to as comprehensive environmental assessment (CEA).

The stability of diesel–bioethanol blends for use in diesel engines was investigated by Lapuerta et al. [151]. They found that high ethanol content in the presence of water at low temperatures causes phase separation, which may be prevented by the addition of a fuel additive. Blends with bioethanol content up to 10% v/v can be used in diesel engines in areas where winter temperatures rarely fall to −5 °C. Blends containing7% bioethanol, such as those used commercially, can be used in even colder areas.

The effects of adding of vegetable methyl ester to diesel–ethanol blends were studied by Chen et al. [152], who observed that the addition of ester to diesel–ethanol blends prevents phase separation up to 30% by volume. Ignition time was delayed with increasing ethanol content and combustion duration, and flame luminosity was decreased. In addition, smoke and PM emissions were reduced with increasing ethanol content. Palm biodiesel has been suggested as an additive for ethanol–diesel blends, in order to maintain the homogeneity of blends [91].

Huang et al. [153] investigated the engine performance and exhaust emissions of a diesel engine fueled with 10%, 20%, 25% and 30% ethanol-blended diesel fuels with and without 5% *n*-butanol as an additive. BTE decreased as the amount of ethanol in the diesel–ethanol blends increased. Smoke emissions were lower when the engine was fueled with the blend compared to neat diesel fuel, while CO emissions were lower at and above half loads, but were higher at low load and low speed. HC emissions were higher except at full loads and high speeds while NO_x emissions varied at different speeds, loads and blends.

Di et al. [154] studied the emissions of a DI diesel engine fueled by ultra-low sulfur diesel with ethanol and biodiesel (2%, 4%, 6% and 8% in volume) used as oxygenated additives. BTE improved slightly as the amount of ethanol and biodiesel in the fuel blends increased, while THC and CO emissions decreased, but NO_x emissions increased compared to those of neat diesel fuel.

The performance and emissions characteristics of 10%, 15%, 20%, 25% and 30% ethanol–diesel blend fuels with 1% isopropanol, as an additive for enhancing homogeneity and preventing phase separation in a DI diesel engine were investigated by Banugopan et al. [155]. The inlet air was preheated to 40, 50 and 60 °C. Total fuel consumption and specific fuel consumption (SFC) increased as ethanol concentration increased, while BTE decreased without preheating. Simultaneously they observed that preheating inlet air had negative effect on CO and HC emissions.

Recently, Hulwan et al. [156] reported that the addition of jatropha biodiesel improved the solubility of ethanol in diesel fuel. The combustion effects were assessed using a multi-cylinder, DI diesel engine with an original injection timing of 13° CA BTDC. Advanced timing was required when there was an increase in the percentage of ethanol in the blend, while advance injection timing almost doubled the NO emissions. Further, BSFC was increased considerably, the thermal efficiency improved slightly, and the smoke opacity was markedly reduced at high loads for blends compared to baseline diesel fuel. NO emissions were dependent on operating conditions, while CO emissions increased dramatically at low loads and decreased slightly at high loads.

In continuation of a previous study [149] related to the use of rapeseed seed methyl and ethyl ester, the effect of adding 5 vol% rapeseed methyl ester (B5E15) to 15 vol% ethanol–diesel blends in a DI diesel engine on BSFC, BTE and emissions were determined and compared with neat diesel fuel. The test results revealed a higher BSFC at 0.7 MPa of BMEP, and a lower BTE at 1400, 1800 and 2200 rpm. However, smoke and NO_x emissions were reduced, while CO_2 emissions were increased [157].

Most recently, the effects of a wide range of concentrations of three kinds of ultralow sulfur diesel (ULSD) blends with ethanol, biodiesel (produced from waste cooking oil), and diglyme (diethylene glycol dimethyl ether) on PM and gaseous emissions were investigated. PM reduction efficiency increases with the addition of ethanol but decreases when diglyme is added. Gaseous emissions such as HC, CO, NO_x and NO_2 increased when ethanol–diesel blends were used, but decreased in the case of diglyme–diesel blends, and were in between for biodiesel–diesel blends [158].

Collectively, these studies demonstrate that ethanol (used in the form of an ethanol–diesel fuel blend, diesel fuel–emulsions or as an oxygen additive) is a promising alternative fuel for use in diesel engines due to advantages including low price and high oxygen fraction. However, the addition of ethanol to diesel increases ignition delay and combustion noise. Therefore, the addition of a small amount of CN improver is helpful for reducing combustion noise. Previous studies examined the utilization of diesel–ethanol blends in a CI engine [136,159,160]. However, these studies concentrated primarily on engine performance and emissions, and little work has examined combustion parameters based on heat release, such as combustion phase analysis and combustion duration analysis, with or without CN improver. The clarification of these parameters may supply more information on

combustion mechanisms in engines fueled with diesel–ethanol blends and enable the determination of practical measures of engine operation.

In this context, Lu et al. [161] compared the effects of ethanol–diesel fuel blends and a CN improver on BSFC, BTE, exhaust emissions (smoke number, CO, NO_x, and THC), and combustion characteristics in a single-cylinder diesel engine. BSFC, BTE and THC emissions were increased, while CO, NO_x, and smoke emissions were decreased. The CN improver had positive effects on CO and NO_x emissions, but a negative effect on THC emissions. Based on the visualization of engine combustion and in-cylinder temperature field analysis by the primary color method, the use of ethanol–diesel blended fuels result in increased ignition delay and decreased total combustion duration, flame luminosity, and the peak combustion temperature.

Kim and Choi [162] studied the performance and emissions of a common-rail direct injection diesel engine, using three different ultra-low sulfur fuels (an ethanol–diesel blend, an ethanol–diesel blend with a CN improver and pure diesel). They observed that the THC and CO emissions of ethanol–diesel blend fuels increased slightly while the smoke emissions decreased by more than 42%. The total number and total mass of the PM were decreased by 11.7–15% and 19.2–26.9%, respectively.

Li et al. [163] assessed the combustion characteristics of a CI engine fueled with diesel–ethanol blends with and without CN improver. At the same brake mean effective pressure (BMEP) and engine speed, the maximum cylinder pressure ($P_{\max}$), ignition delay, premixed combustion duration, and fraction of heat release in the premixed combustion phase increased, while the diffusive combustion duration, fraction of diffusive combustion phase, and total combustion duration decreased as the ethanol fractions in the blends increased. The center of the heat release approached the top dead center (TDC), and the maximum rates of heat release and pressure rise increased when ethanol fraction in the blends was increased. In addition, the addition of CN improver to diesel–ethanol blends alleviates the decreases in ignition delay, cylinder peak pressure, maximum rate of pressure rise, and combustion noise.

Sahin et al. [164] found that BSFC increases with increasing ethanol ratio at a constant equivalence ratio (CER). Additionally, the brake effective power, brake effective efficiency, and combustion duration increased with 4–6% ethanol blends at CER, and decreased at higher ethanol concentrations. CO and H_2 emissions exhibited decreasing tendencies, but NO emissions increased at low ethanol ratios and began to decrease at high ratios. Ethanol blends were not economical at CER due to the increase in BSFC.

The effect of a CN improver [2-ethylhexyl nitrate (EHN, $C_{10}H_4C_{l3}$–NO_2)] on the combustion and emission characteristics of a CI engine fueled with an ethanol–diesel blend was reported by Liu et al. [165], who found that BTE, diffusive combustion phase, and total combustion duration were increased by increasing CN improver content, while the ignition delay was decreased. The additions of ethanol and a CN improver to diesel had no effect on NO_x emissions, while the PM and smoke emissions from the E30 blend decreased significantly, and were expected to decrease further with increasing amounts of CN improver.

Recently, Park et al. [166] assessed the combustion and emission characteristics of bioethanol–diesel blended fuel. Experiments were conducted under various bioethanol blending ratios (E10, E20 and E30), injection timings, and EGR ratios (0%, 20% and 40%) in a naturally aspirated, single-cylinder DI diesel engine. Increasing amounts of bioethanol in the blend extended the ignition delay because of the low CN and decreased gas temperature. The differences in ignition delay between pure diesel fuel and diesel-bioethanol blended fuels became larger under early injection conditions, while NO_x and soot emissions were reduced as amount of bioethanol increased and the use of EGR and bioethanol-diesel blending further increased NO_x emissions. On the other hand, HC emissions increased as the amount of bioethanol increased and the injection timing was advanced.

Rakopoulos et al. [167] conducted an experimental study to evaluate the effects of diesel fuel with either 5% and 10% ethanol or in 8% and 16% *n*-butanol (by vol.), on the combustion behavior of a fully-instrumented, six-cylinder, Mercedes-Benz DI engine under three loads and at two engine speeds (1,200 and 1,500 rpm). The use of ethanol or butanol resulted in slight decreases in the pressure diagram and an increase in ignition delay, a slight delay in maximum cylinder pressures, and a reduction in cylinder temperatures compared to pure diesel fuel. However, the smoke opacity and NO_x emissions decreased with increasing ethanol and butanol in the blends.

Park et al. [168] studied the spray, combustion and exhaust emissions characteristics of a commercial four-cylinder diesel engine, fueled with pure diesel and an ethanol–diesel fuel blend. The ethanol blended diesel fuel has a shorter spray tip penetration than pure diesel fuel. In addition, a high ethanol blending ratio induced a large reduction rate in spray tip penetration due to a decrease in fuel density. Ethanol blended fuels had larger spray cone angles than pure diesel fuel. Unstable ignition characteristics were observed when ethanol blended diesel fuels were injected around TDC. In addition, advancing the injection timing led to an increase in combustion pressure. There was a decrease in NO_x emissions when the amount of ethanol in the diesel–ethanol blend was increased. However, NO_x emissions increased as the engine load and injection timing increased. CO and HC emissions increased with an increase in ethanol blending ratio. On the other hand, low NO_x and high CO and HC emissions were observed at low engine loads.

Due to the low CN of ethanol, ethanol–diesel fuel blends may cause cyclic variability (irregularity) in diesel engines. Rakopoulos et al. [169] carried out an experimental investigation to evaluate the use of ethanol as a supplement to conventional diesel fuel at blend ratios of 5E, 10E and 15E in a DI engine working at a speed of 2,000 rpm under four different loads. The use of ethanol blends instead of neat diesel fuel resulted in an increase in ignition delay and, a slight decrease in fuel injection pressure, while the rate of maximum pressure increase and maximum cylinder pressures were only slightly affected. Further, the pressure in the fuel pipeline in relation to the ignition delay and, the fuel system had no influence on cyclic pressure variation. This pattern also holds true for the influence of fuel types (with different CNs), at least for low ethanol content (up to 15%) in diesel fuel blends, thus ensuring that the type of fuel used will not degrade performance or emissions characteristics.

Further, the effects of ethanol fumigation on engine performance and emissions have been studied by several investigators [170–174]. Alcohol fumigation is a form of dual-fuel engine operation in which alcohol is premixed with intake air by injection or vaporization of alcohol, while the diesel fuel is injected directly into the cylinder as in a traditional diesel engine. Fumigation requires minor modifications of the engine so that alcohol can be injected into the air intake using low-pressure fuel injectors. Ethanol fumigation caused significant reductions in smoke, PM and NO_x emissions, while HC and CO and NO_2 emissions were increased and no significant changes in CO_2 emissions were observed. Thermal efficiency was not affected, but a slight reduction in BTE was noted. The use of DOC reduced CO, HC, and PM emissions when the exhaust gas temperature was sufficiently high. The dramatic reduction in NO_x emissions suggests that fumigation may serve as an emission control technique in diesel engines. The fumigation and blending methods have similar influence on performances and emissions.

Table 4
Summary of ethanol–diesel blend studies dealing with performance and emissions of diesel engine.

Reference	Engine type	Ethanol (%)	Stability additive (%)	Reference fuel	Emissions	Performance	Others parameters
He et al. [8]	4-cylinder DI diesel engine	10 30	1 2	Diesel	▲:CO, MeCHO ▼:CO_2, Smoke, NO_x ▼:CO, MeCHO, THC[f]	▼:CN	Ignition improver, additives
Caro et. al. [9]	Single cylinder DI and 4-cylinder IDI engines	10 15 20	2	Diesel	▲:HC ▼:Smoke, CO —:NO_x	▼:CN, Power, heat contents	Additives
Shi et. al. [10]	4-cylinder DI diesel engine	3 4	6 12	Diesel	▲:NO_x, THC ▼:Smoke, PM, CO	n/a	Additives
Xing-cai et al. [11]	4-cylinder, naturally aspirated high-speed DI diesel engine	15	0.2 0.4	Diesel	▲:CO ▼:NO_x, Smoke, HC	▲:BSFC, Thermal efficiency, ignition delay	CN improver
Lei et al. [93]	4-cylinder, naturally aspirated water-cooled 4-stroke DI diesel engine	5 10 15	0.8 1 1.5	Diesel	▲:CO[d], THC[d] ▼:NO_x[b], CO[b], Smoke[b]	▲:BTE ▼:BSEC	Emulsifiers
Likos et al. [129]	6-cylinder TDI diesel engine	10 25 50	10 15 20	D-2 Diesel	▲:NO_x ▼:HC, CO ▲:CO[b], HC[b]	n/a	Ignition improver, engine load
Pischinger et. al. [130]	Single cylinder swirl chamber diesel engine	25	5	Diesel	▲:CO[d], HC[d] ▼:CO[b], HC[b], NO_x[b]	n/a	Ignition improver, engine load
Jiang et. al. [131]	4-cylinder turbocharged diesel engine	n/a	No	1#2 Diesel	▼:NO_x	n/a	Engine speed and load
Cole et al. [132]	Volkswagen TDI diesel engine	10 15	No	#2 Diesel	▼:PM, NO_x, HC,CO	n/a	Engine speeds and torque
Kass et. al. [133]	5.9 l ISB TDI diesel engine	10 15	2	LSD	▲:CO, THC ▼:PM —:NO_x	n/a	Engine load
Koganti et. al. [134]	4-stroke water-cooled 3-cylender DI diesel engine	5	Yes (n/a)	Diesel	▲:NO_x ▼:CO, PM	▼:Power output, fuel economy ▲:BSFC, Thermal efficiency, ignition delay	CN improver, engine speed
Ajav et. al. [135]	Single cylinder 10 hp (7.4KW), constant speed CI engine	5 10 15 20	No	HSD	▼:CO, NO_x	▲: BSFC, $T_{exhaust}$ ▼: BTE —: power	Engine load
Bilgin et. al. [136]	Single cylinder 4 stroke variable compression ratio engine	2 4 6	No	Diesel	n/a	▲:BTE, Break torque and power ▼: BSFC	Compression ratio
Li et. al. [137]	Water-cooled single-cylinder DI diesel engine	5 10 15 20	1.5	Diesel	▲:THC ▼:Smoke, CO, NO_x	▲:BSFC, BTE	Engine load
Rakopoulos et al. [138]	6-cylinder, turbocharged and after-cooled HDDI Mercedes-Benz engine	5 10	1.5	LSD	▲:UHC ▼:Smoke, CO —:NO_x	▲:SFC, BTE	Engine speed and load
Arapatsakos et al.[139]	4-cylender John Deer Tractor engine	20 30	No	Diesel	▼:CO, HC	▼:Power	Engine speed and load
Rakopoulos et al. [140]	Single-cylender four-stroke HSDI 'Hydra' diesel engine	5 10 15	1.5	LSD	▲:UHC ▼:NO_x, CO	▲:SFC, BTE ▼:$T_{exhaust}$	Engine speed and load
Song et al. [141]	6-cylender, heavy-duty non-catalyst turbocharged inter-cooler DI diesel engine	15	0.3 1.2	Diesel	▲:HCHO, MeCHO, $(CH_3)_2$ CO, Crotonaldehyde, propionaldehyde ▼:Acrolein[b]	n/a	Engine speed
Lei et al. [142]	3.298 L 4-stroke TDI diesel engine	10, 15 20, 30	No	Diesel	▲:HC, CO ▼:NO_x, Smoke	▼:SFC	Atmospheric pressure
Boruff et al. [144]	Ford 2000 naturally aspirated DI diesel engine	16	4.1 12.5	Diesel No.2	▲:Unburned HC ▼:Smoke, CO	▲: BTE ▼: $T_{exhaust}$	Surfactants

Table 4 (*continued*)

Reference	Engine type	Ethanol (%)	Stability additive (%)	Reference fuel	Emissions	Performance	Others parameters
Bhattacharya et al.[145]	Constant speed direct-injection diesel engine rated at 7.4 kW	11 17	27.8 33.3	Diesel	▲:UHC, NO_x ▼:CO	—:Density, viscosity, gross heat of combustion	Ethanol-1-butanol–diesel micro-emulsions
Kumar et al. [146]	Direct injection single cylinder air-cooled naturally aspirated CI engine	13 17 23	7 13 17	Diesel	▲:HC[d], CO[d] ▼:NO_x[b], Smoke[b], UHC[b], CO[b]	▲:BSFC ▼:BSEC, Thermal efficiency	Emulsions
Ganesh et al. [147]	Single cylinder water-cooled 4-stroke DI diesel engine	30 40 50	Yes (n/a)	Diesel	▲:NO_x ▼:PM, Smoke;	▲:BTE, Ignition delay ▼:$T_{exhaust}$	Injection angles
Can et al. [148]	4-cylinder indirect injection, turbocharged diesel engine	10 15	Yes (n/a)	Diesel No.2	▲:NO_x ▼:CO, Soot, SO_2	n/a	Engine load and speed
Chen et al. [152]	4-cylinder Cummins type engine	10 20 30	5 10	Diesel	▲:NO_x ▼:Smoke, PM	▼:Ignition delay, combustion duration, flame luminosity	–
Huang et al. [153]	Single-cylinder 4-stroke water-cooled DI compression-ignition engine	10 20 25 30	5	Diesel	▲:CO, HC ▼:smoke, NO_x ▲:NO_x[c]	▲:BSFC —:BTE	Engine load
Di et al. [154]	Naturally aspirated 4-cylinder DI diesel engine	2 4 6 8	No	ULSD	▲:HC[d], CO[d], NO_x[d] ▲:NO_2, HCHO, MeCHO ▼:NO[d] ▼:BTX	▲:BTE	O_2 concentrations (2%, 4%, 6%, 8%)
Banugopan et al. [155]	Single cylinder 4-stroke water cooled diesel engine	10, 15 20, 25 30	1	Diesel	▲:HC, CO	▲:SFC ▼:BTE	Engine loads
Hulwan et al. [156]	Multi-cylinder, DI diesel engine	20 30 40	10 20	Diesel	▲:HC, CO ▼:NO	▲:BSFC, Thermal efficiency	Injection timing, biodiesel
Labeckas et al. [157]	4-cylinder 4 stroke naturally aspirated DI diesel engine	15	5	Diesel No.2	▲:CO_2, UHC ▼:NO_x, smoke, CO	▲:BSFC ▼:BTE	Rpm, air to fuel ratio
Wang et al. [158]	4-cylinder naturally Aspirated water-cooled DI diesel engine	2 4 6 8	1 1.5	ULSD	▲:HC, CO, NO_x, NO_2 ▼:HC, CO, NO_x, NO_2[g]	n/a	Diglyme (DGM), O_2 2%, 4%,6% 8
Ren et al. [159]	Compression ignition DI diesel engine	5 10 15 20	0.2	Diesel	▼:Smoke, NO_x,	▲:Ignition delay, combustion duration, heat release, ▼:BSFC	Crank angle
Lu et al. [160]	4-cylinder 4-stroke, naturally aspirated water-cooled, DI diesel engine	5 10 15 20	0.2 0.4	Diesel	▲:HC ▼:NO_x, CO ▼:CO[e], HC[e]	▲:BTE ▼:Ignition time, combustion	CN improver
Lu et al. [161]	Single-cylinder DI diesel engine	5, 10, 15, 20	1.5	Diesel	▲:THC ▼:Smoke, CO, NO_x	▲:BSFC, BTE	CN improver, engine load
Kim and Choi [162]	4-cylinder common-rail DI diesel engine	15	2	ULSD	▲:THC, CO ▼:Smoke, PM	▲:BSFC ▼:BTE	–
Li et al. [163]	Single-cylinder DI diesel engine	5 10 15 20	0.2	Diesel	n/a	▲:P_{max}, Ignition delay, heat release ▼:combustion duration	CN improver
Sahin et al. [164]	DI diesel engine	2 4 6 8 10	No	Diesel	▲:NO ▼:CO, H_2	▲:BSFC, Brake effective power and efficiency	Modeling, equivalence ratio, compression ratio

Liu et al. [165]	4-stroke water-cooled DI diesel engine	30	0.3 0.6	commercial China 0 diesel	▼:CO, HC —:NO_x	▲:BTE ▼:BSFC	Engine load
Park et al. [166]	Single-cylinder naturally aspirated DI diesel engine	10 20 30	5	ULSD	▲:HC ▼:NO_x, Soot	▲:Ignition delay	EGR, injection timing
Rakopoulos et al. [167]	6-cylinder turbocharged after-cooled HD DI (Mercedes-Benz) engine	5 10	1.5	LSD	▼:Smoke, NO_x,	▼:Ignition delay, cylinder temp., P_{max}	Fuel delivery angle, engine load
Park et al. [168]	4-cylinder diesel engine with a common-rail injection system.	10 20	10	ULSD	▲:HC, CO ▼:NO_x ▲:NO_x[b] ▼:HC[d], CO[d], NO_x[d]	▲:Ignition delay	Injection timings, engine load
Rakopoulos et. al. [169]	Single-cylinder 4-stroke water-cooled Ricardo-Cussons 'Hydra' engine	5 10 15	1.5	LSD	n/a	▲:Ignition delay, maximum pressure rates —: P_{max}	Injection timings, engine load
Tsang et al. [170]	4-cylinder naturally aspirated DI diesel engine	5 10 15 20	No	Euro V diesel fuel	▲:HC, CO, NO_2 ▼:NO_x, Smoke, PM ▼:HC[a], CO[a], NO_x[a]	▲:BSFC, Ignition delay, P_{max} ▼: BTE	Fumigation, DOC, engine load
Sahin et al. [171]	DI diesel engine	2.5, 5 7.5, 10 15, 20	No	Diesel	▲:CO ▼:NO	▲:Effective power, effective efficiency ▼:SFC	Theoretical study, fumigation
Janousek et al. [172]	John Deere 4.5 L Power Tech Plus 4 valve head Tier 3 diesel engine	60 80 100	No	Diesel No.2	▲:HC, CO ▼:NO_x,	▲:BSFC —:BTE	Fumigation, engine speed and load
Chauhan et al. [173]	Small capacity DI Kirloskar diesel engine	10, 20 30, 40 50	No	Diesel	▲:HC, ▼:CO, NO_x, CO_2, Smoke	n/a	Fumigation, engine load
Surwski et al. [174]	4-cylinder Ford 2701C test engine	10, 20, 40	No	Diesel	▲:HC, CO ▼:PM, NO	n/a	Fumigation, engine loads, DOC
Can et al. [175]	4-cylinder (Ford XLD 418 T) 4- stroke water-cooled turbocharged IDI engine	10, 15	1	Diesel no. 2	▲:NO_x ▼:CO, smoke, SO_2	n/a	Injection pressure

▲, Increase; ▼, Decrease; —, no change; n/a, not available.

[a] effect of diesel oxidation catalyst.
[b] at high load.
[c] at high speed.
[d] at low load.
[e] effect of CN improver.
[f] effect of ignition improver.
[g] effect of diglyme.

Moreover, Can et al. [175] investigated the impacts of ethanol (10% and 15% volume)–diesel fuel blends on diesel engine emissions using different injection pressures (150, 200 and 250 bars) under a full load. Increasing the injection pressure of an engine fueled with an ethanol–diesel blend decreased CO emissions and smoke opacity while NO_x emissions were increased. The results of each investigation related to the combustion, performance and emissions of ethanol–diesel fuel blends in different engines are summarized in Table 4.

5.2.1. Summary and future research directions

The reported investigations reveal that the addition of ethanol to diesel fuels affects important properties such as the cetane number, heat of combustion, stability, and lubricity. Therefore, ethanol–diesel fuel blends must be formulated with extreme preciseness. The use of effective and economical additives is essential for maintaining the homogeneity of blends in storage and for restoring the quality of ignition and the lubricity of the original diesel fuel. The additions of butanol and vegetable oils increase the stability of ethanol–diesel blends and enhance engine performance while reducing emissions. The addition of CN improver reduces the cyclic variability associated with the use of E-diesel. Further, in order to enhance the miscibility of ethanol in diesel fuel and to enhance the fuel properties of E-diesel, the use of butanol and biodiesel as additives should be further explored. By adhering to these guidelines, it is possible to synthesize stable E-diesel fuel that may substitute for diesel with only a slight penalty in fuel economy.

Moreover, the studies reviewed in this section indicate that the increasing use of ethanol blends will lead to losses in engine power, mainly due to the reduction in heating value associated with fuel blends. In most of the researches an increase in fuel consumption were observed, due to the LHV of ethanol. Significant reductions in CO, PM and NO_x emissions with slight penalties in HC were observed by majority of investigators. However, some studies reported that HC decreases while other emissions increase with increasing amounts of ethanol in fuel blends. The engine load, engine speed, injection timing and injection pressure also play significant roles in engine performance and emissions. E-diesel may be a suitable replacement for diesel fuel in controlling air pollution and easing the pressure on scarce resources without significantly sacrificing engine power or economy.

A method for producing ethanol from cellulosic feed-stock using new and advanced technologies should be developed to increase the commercial use of ethanol and reduce its cost. In addition, few studies have examined the use of ethanol–diesel blends under low temperature conditions (e.g., $-5\,^{\circ}C$ or lower) [151]. Hence, further experiments at lower temperatures ($-15\,^{\circ}C$, $-35\,^{\circ}C$) are required to determine the optimum percentage of ethanol in E-diesel, the stability of E-diesel at lower ambient temperatures (-10, $-35\,^{\circ}C$), and the role of different additives. Moreover, research related to the effects of injection timing and pressure on engine performance and emissions should be conducted for E-diesel.

5.3. Butanol–diesel fuel blends

n-Butanol is a strong competitor as a fuel additive for diesel engine, the use of which has rarely been investigated in diesel engines. Unlike shorter chain alcohols, butanol has the potential to perform well as a gasoline surrogate, and has a moderate cetane number, which allows for the incorporation of significant amounts of butanol in diesel fuel [64]. Butanol is of particular interest as a renewable biofuel, as its properties are much more similar to diesel fuel than are those of ethanol [176].

Under current US Environmental Protection Agency regulations, biobutanol can be blended as an oxygenate with gasoline at concentrations up to 11.5% by volume. However, in the near future, butanol may become a suitable substitute for fossil fuels, not only as a blend, but on its own. The production of butanol from agricultural feedstocks and its consumption as a precursor for a diverse set of fuel products may decrease petroleum usage globally. However, few studies have been performed to investigate butanol–diesel fuel blends as an alternative fuel for diesel engines with respect to engine performance and emissions [177–179].

Miers et al. [177] investigated the performance and emissions of a Mercedes-Benz C220 turbo diesel vehicle fueled with butanol–diesel blends (20% and 40% by volume). For the urban drive cycles, HC and CO emissions were increased as the amount of butanol in the butanol–diesel blend increased. The 20% butanol blend did not significantly affect NO_x emissions, which were increased by the 40% butanol blend. Vehicle drivability decreased when the 40% butanol blend was used. Fuel consumption increased with increasing amounts of butanol. The results for the highway drive cycle were opposite those for the urban drive cycle.

Rakopoulos et al. [178] studied the effects of *n*-butanol (8%, 16% and 24%)–diesel fuel blends on the performance and emissions of a high speed DI diesel engine operating at a speed of 2000 rpm under three different loads (low, medium and high). Smoke density was significantly reduced while NO_x and CO emissions were slightly reduced with the use of the butanol–diesel fuel blends compared to the neat diesel fuel. However, the HC emissions increased with the use of the butanol–diesel fuel blends. As the percentage of butanol in the blends increased, marginally higher specific fuel consumption was observed with a correspondingly slight increase in BTE at slightly lower exhaust gas temperatures.

Rakopoulos et al. [179] investigated the performance and emissions of a six-cylinder, water cooled, turbocharged heavy duty Mercedes-Benz DI engine operating on butanol (8% and 16%)–diesel fuel blends. A series of tests at two speeds (1,200 and 1,500 rpm) and under different loads (3.56, 7.04 and 10.52 brake mean effective pressure (BMEP)) yielded results similar to those of a previous study [178]. Further, an experimental study was performed by Yao et al. [180] to determine the effects of diesel fuel and *n*-butanol content on the performance and emissions of a heavy-duty DI diesel engine, with multi-injection fuel capability. The exhaust gas recirculation rates were adjusted to ensure that the NO_x emissions remained constant. The addition of oxygenated *n*-butanol considerably decreased soot and CO emissions without any serious influence on BSFC and NO_x.

Taken together, the results of the referenced studies indicate that smoke, NO_x and CO emissions are significantly reduced when butanol–diesel fuel blends are used compared to neat diesel fuel, while HC emissions are increased. Additionally, as the percentage of butanol in the blends increased, slightly higher specific fuel consumption was observed with a corresponding minor increase in BTE.

The effects of adding *iso*-butanol to diesel fuel on engine performance were investigated by Al-Hasan et al. [181]. The tests were performed at engine speeds ranging from 375 to 625 rpm under different loads with10, 20, 30 and 40% (v/v) *iso*-butanol–diesel blends. As the engine speed increased, the exhaust gas temperature, brake power and BSFC increased while the BTE and air fuel ratio decreased. They found that up to 30% *iso*-butanol can be added to diesel fuel to achieve desired engine performance, while the addition of 40% *iso*-butanol resulted in deviations in engine performance.

Further, variations in the engine performance and exhaust emissions of a diesel engine using *iso*-butanol–diesel fuel blends

were investigated by Karabektas [182] et al. and were compared to those of neat diesel fuel. Blends containing 5%, 10%, 15% and 20% *iso*-butanol were prepared and tested under full -load conditions at speeds ranging from 1,200 to 2,800 rpm at intervals of 200 rpm. All blends resulted in a diminished BTE and break power proportional to the *iso*-butanol content. Among the blends verified, the maximum BTE was attained with 10% *iso*-butanol. The use of *iso*-butanol–diesel fuel blends caused decreases in CO and NO_x emissions while HC emissions increased. As *iso*-butanol content increases in *iso*-butanol–diesel fuel blends, engine power, BTE, and exhaust gas temperature decrease while BSFC increases [181–182].

Another study [183] revealed that a decline in smoke density occurred when an *iso*-butanol–diesel fuel blend was used compared to neat diesel fuel. Further, decrements in smoke concentration were noted when *iso*-butanol was added to diesel-olive oil mixtures. Adding 5–10% *iso*-butanol to 10% olive oil–diesel further reduced smoke, CO and HC emissions.

Ozsezen et al. [184] recently evaluated the impacts of *iso*-butanol (5%, 10% and 15%)–diesel fuel blends on the performance and combustion of a heavy duty diesel engine working at a speed of 1,400 rpm for three different loads (150, 300 and 450 Nm). BSFC was increased and was moderate when 5 and 10% *iso*-butanol were used, but was the highest with 15% blend. BTE was decreased in proportion to *iso*-butanol content. Peak cylinder gas pressure and heat release rate were slightly increased compared to neat diesel fuel, while smoke opacity, NO_x and CO emissions were considerably reduced with the use of *iso*-butanol–diesel fuel blends. However, HC emissions were slightly increased.

An experimental study of the performance and soot emissions characteristics of a high-speed inter-cooled diesel engine fueled with butanol (0%, 20% and 30%)–diesel blended fuel was executed by Biao et al. [185], who reported that 30% butanol had slight effects on maximum brake power and maximum brake torque. However, soot emissions were significantly reduced when a 30% butanol fuel blend was used compared to a 20% butanol blend.

Further, Dogan [186] investigated the performance and exhaust emissions of a single cylinder, four-stroke, naturally aspirated DI diesel engine at a constant engine speed (2,600 rpm) under four different engine loads using *n*-butanol (5%, 10%, 15% and 20%) blended diesel fuel, and found that BSFC and BTE were slightly increased with increasing *n*-butanol content in fuel blends while exhaust gas temperature, NO_x, smoke opacity and CO emissions were reduced. However, HC emissions were increased as shown in.

Rakopoulos [187] recently examined the combustion of *n*-butanol (8%, 16% and 24% by volume)–diesel fuel blends in a DI diesel engine. The type of engine and operating conditions were similar to those examined in the previous study [179]. The use of *n*-butanol blends increased ignition delay, caused delays in fuel ignition pressure diagrams, did not significantly affect the maximum cylinder pressure, and slightly decreased the cylinder temperature, compared to neat diesel fuel. A slight increase in BTE resulted in significant reductions in smoke density and NO_x emissions when *n*-butanol–diesel fuel blends were used rather than neat diesel fuel.

In another study, Rakopoulos et al. [167] investigated the combustion behavior of a six-cylinder, heavy duty, turbocharged DI engine, fueled with either ethanol (5% and 10%) or *n*-butanol (8% and 16%)–diesel fuel blends. Ethanol and *n*-butanol fuel blends were similar in terms of emissions, but the ethanol fuel blends decreased smoke density while *n*-butanol fuel blends decreased the NO_x emissions more than the ethanol blends. BSFC and BTE were higher for the 8% and 16% *n*-butanol blends, at engine speeds of 1,200 rpm and 1,500 rpm, compared to pure diesel fuel. The fuel injection pressure diagrams were slightly delayed. Ignition delay was increased and the maximum cylinder pressure was slightly reduced. The cylinder temperature was reduced during the first part of combustion.

The combustion of low CN fuels may cause significant cyclic variability (cycle-to-cycle cylinder pressure variations) in CI engines, which degrades the engine performance and reliability, increases engine noise and exhaust gas emissions, and causes power fluctuations. Due to this variability, scatter of separate cylinder pressure curves around the phase averaged mean may arise rather than spotting the same time progression of the cylinder pressure for all phases. As a consequence, the work exhibited by each separate cycle varies from the mean work, which is the design objective of engine manufacturers. In severe cases, incomplete burns or misfires may take place. Higher variability may have adverse effects on the driveability and can lead to increased pollutant emissions and fuel consumption.

Cycle-to-cycle combustion variation has been effectively investigated over the last few decades [188]. A review by Ozdor [189] suggests that the removal of cycle-to-cycle inconsistency could lead to a 10% increase in power output for the same amount of fuel. Predicting and controlling cyclic variability is thus a critical technical issue for engine designers.

Important studies related to cycle-by-cycle pressure variation in diesel engines were conducted by Wing [190], Koizumi et al. [191], Sczomac and Henin [192] and Kouremenos et al. [193]. These studies extensively investigated pressure variation in single-cylinder engines operating on diesel fuel, under various loads and injection timings, using stochastic techniques, and found no correlations between cyclic pressure variations and injection system type.

However, Table 2 shows that most of the physicochemical properties of butanol are similar to those of diesel fuel and gasoline. Undoubtedly the CN of butanol is higher than those of methanol and ethanol, but is lower than that of diesel fuel. The addition of butanol to diesel fuel can decrease the CN of butanol–diesel fuel blends and may result in cyclic variability problems.

In this context, Rakopoulos et al. [187] investigated the combustion of *n*-butanol–diesel fuel blends and cyclic variability in a DI diesel engine via statistical analysis of cycle-by-cycle variations in measured engine combustion parameters. The fluctuation phenomenon in cyclic variability was random for this type of engine. An analysis of pressure in the fuel pipeline with respect to ignition delay showed that the type of fuel pump system used has no impact on cyclic pressure variation. This observation holds true for the effects of fuel type (with different CNs), at least for low *n*-butanol content (up to 24% by volume) diesel fuel blends, thus confirming that *n*-butanol does not degrade performance or emissions.

Yao et al. [194] studied the effects of EGR on the efficiency and emissions of a heavy duty diesel engine using B10 and B20 blends by varying combustion parameters such as injection pressure and timing, compression ratio, and boost. Oxygenated diesel fuel demonstrated the potential to reduce soot and NO_x emissions. EGR was determined to be an important parameter for controlling diesel engine combustion. With higher injection pressure, higher boost pressure and oxygenated fuel, medium EGR was found to be more suitable for controlling emissions and enhancing engine performance when compared to heavy and low EGR ratios.

Further, Tornatore et al. [195] examined the combustion effects of commercial diesel fuel and a blend of 80% butanol with 20% diesel fuel in an optically assessed high swirl multi-jet CI engine. Combustion process was studied from the injection to the late combustion phase. This process was studied at a fixed injection pressure of 70 Mpa by varying the injection timing and EGR rate. The blends increased ignition delay, particularly at late injection timing. Major reductions in smoke and NO_x were

obtained with slight penalty on engine efficiency. To overcome this constraint, a mixing controlled combustion low-temperature combustion (LTC) regime was realized by using an earlier injection and a B20 blend at 50% of EGR, and late injection timing was found to significantly reduce engine emissions.

These studies reveal that EGR and injection timing significantly affect combustion conditions, which in turn affects fuel economy. The analysis of in-cylinder pressure and corresponding heat release rate also provide basic information about the combustion process. It is observed that peak cylinder gas pressure, heat release rate and ignition delay generally increase with increasing amounts of butanol or *iso*-butanol in butanol/*iso*-butanol–diesel fuel blends compared to neat diesel fuel. Due to the self-ignition temperature and low CNs of butanol and *iso*-butanol, which do not ignite as easily as diesel fuel do, ignition delay increases with increasing amounts of butanol. Engine load has also been found to have a significant impact on the combustion behavior of fuel. Normally, with increasing engine load, fuel consumption increases and the volume of combustible fuel also increases in the combustion compartment. This in turn increases the peak point of heat release with increasing load. Heat release analysis reveals important impacts of engine design changes, fuel injection system, fuel type, and engine operating conditions on the combustion process and engine performance [184]. Additionally, the combustion of butanol–diesel blends may lead to better thermal efficiency and less heat loss than neat diesel fuel, while and soot and NO_x emissions were reduced significantly.

In addition to diesel–butanol blends, alcohol–vegetable oil (biofuel) blends also have strong influences on the emissions and performance of a diesel engine. In this context, Yosimoto et al. [196,197] studied the addition of oxygenated organic compounds (alcohols) to rapeseed oil. The addition of 1-propanol or 1-butanol to rapeseed oil resulted in stable combustion much like that observed with gas oil, and alcohol blended fuels showed lower smoke emissions, unchanged NO_x emissions and slightly higher BSEC [196]. Completely miscible mixtures were obtained when up to 29% 1- propanol, 1-butanol or 1-pentanol was added [197]. The combustion, performance and emissions results were similar to those of previous study [196]. A strong negative correlation was observed between smoke density and oxygen content of the fuel when neat rapeseed oil was used in both studies.

Lujaji et al. [198] evaluated the effects of croton oil, diesel fuel and butanol blends on the performance, combustion and emission characteristics of a CI engine. They found that the fuel properties of vegetable oils are improved when butanol and diesel fuel were added to vegetable oil. BSFC was increased and BTE was decreased at higher engine loads when the percentage of butanol in the blend was increased. The addition of butanol to croton oil and diesel blend resulted in high cylinder pressure and improved heat release rate compared to diesel fuel, while the CO_2 and smoke emissions of the butanol blend were reduced, and NO_x emissions of the blends were similar to those of neat diesel fuel.

Altun et al. [199] conducted an experimental study to estimate the effects of *n*-butanol addition to blends of diesel and biodiesel on the performance and exhaust emissions of a four-stroke, naturally aspirated, single cylinder direct injection CI engine working at a constant speed (2,000 rpm) under three different loads (6.5 Nm, 11.6 Nm and 17.8 Nm). The addition of *n*-butanol to the diesel–biodiesel fuel blend (B20) caused a slight increase in the BSFC and BTE in comparison to the diesel–biodiesel (B20) fuel blend. The CO and HC emissions were decreased, and the NO_x emissions remained almost unchanged at low engine loads, while they were decreased at high engine loads. The fuel blends also caused a sharp decline in smoke opacity over the entire range of engine tests.

Rakopoulos et al. [200] investigated the effects the addition of biodiesel and *n*-butanol to diesel fuel in the operation of a turbocharged diesel engine. They found that: (I) turbocharger lag was the major contributor to all starting discrepancies and peak pollutant emissions for both blends, (II) low cranking speed had a dominant effect on combustion noise development, (III) combustion behavior and stability were more affected by the biodiesel blend than by the *n*-butanol blend, (IV) smoke opacity was increased for the bio-diesel blend, while it was decreased significantly for the *n*-butanol blend, (V) NO emissions of both biofuel blends were increased compared to neat diesel fuel, and (VI) biofuel blends had minor effect on the transient performance of the engine and overall combustion noise radiation.

To investigate smoke and NO formation mechanisms under various accelerating conditions in turbocharged diesel engines, three fuel blends (30% biodiesel, 25% *n*-butanol and diesel fuel) were verified, and smoke emissions were reduced the most when 25% *n*-butanol blended fuel was used [201]. NO emissions were increased when biodiesel fuel blends were used compared to neat diesel fuel, while they were decreased when an *n*-butanol blend was used. The reduction in smoke opacity values (peak or cumulative values) was greater for the *n*-butanol blend than the biodiesel blend.

Further, the combustion behavior of *n*-butanol has been compared with those of other biofuels. Liu et al. [202] studied the combustion characteristics and soot distributions of neat butanol and neat soybean biodiesel at different ambient temperatures (800 and 1,000 K) and oxygen concentrations (21%, 16%, and 10.5%). The combustion pressure of butanol was lower than that of soybean biodiesel, but butanol had a higher normalized peak pressure, indicating that butanol had higher potential thermal efficiency. However, butanol was found to have lower flame luminosity than soybean biodiesel. The net soot release was increased for both fuels as ambient temperature increased. Further, natural flame luminosity and soot emissions at 1,200 K are reported by Jin et al. [203], who also reviewed the use of butanol as a gasoline additive has been reviewed in this article. The reported investigations related to the combustion, performance and emissions of *n*-butanol/*iso*-butanol–diesel blends are summarized in Table 5.

5.3.1. Summary and future research directions

The available reviews indicate that smoke, NO_x and CO emissions were significantly reduced while HC emissions increased with use of the butanol–diesel fuel blends compared to neat diesel fuel. In contrast, some studies reported that fewer hydrocarbons were emitted. However, other studies reveal that butanol–diesel blends are capable of decreasing soot emissions, while variation in NO_x emissions depends on butanol content and engine operating conditions. These discrepant results may be due to the use of different analytical techniques and engine make-ups. The majority of studies agree that fuel consumption increases and BTE decrease with increasing butanol or *iso*-butanol content. The increase in butanol–diesel fuel consumption is mainly due to the lower heating value of butanol. However, the use of turbocharged or low heat release engines may improve butanol or *iso*-butanol–diesel fuel economy [179]. A few studies of addition of butanol to diesel-biodiesel blends have been reported in literature. In these studies, although the addition of butanol enhances blend properties, it also increases BSFC. However, CO and HC emissions decrease when butanol is added to diesel-biodiesel blends, with a slight penalty on NO_x emissions.

Therefore, *n*-butanol is a promising next generation fuel that can be used safely at high mixing ratios with diesel fuel in diesel engines, with favorable thermal efficiency and exhaust emissions as well as higher CN and better miscibility in diesel fuel than that that of lower alcohols. The main drawback of *n*-butanol is its lower

Table 5
Summary *n*-butanol/*iso*-butanol–diesel blend studies dealing with performance and emissions of diesel engine.

Reference	Engine type	*n*-butanol/*iso*-butanol (%)	Stability additive (%)	Reference fuel	Emissions	Performance	Others parameters
Rakopoulos et al. [167]	6-cylinder turbocharged after-cooled HDDI diesel engine (Mercedes-Benz)	*n*- butanol (8,16)	No	LSD	▼: Smoke, NO_x,	▲:BSFC, BTE, Ignition delay, cylinder temp., P_{max}	Engine load and speed
Miers et al. [177]	4-cylinder common rail DI diesel engine (Mercedes-Benz C220 turbo)	*n*-butanol (20, 40)	No	ULSD	▲:HC, CO, NO_x	▲:BSFC	–
Rakopoulos et al. [178]	4-stroke high-speed DI (Ricardo/Cussons 'Hydra') diesel engine	*n*-butanol (8,16, 24)	No	LSD	▲:UHC ▼:Smoke, NO_x, CO	▲:BTE,SFC ▼:$T_{exhaust}$	Engine load
Rakopoulos et al. [179]	6-cylinder 4-stroke water-cooled HDDI diesel engine (Mercedes-Benz, OM 366 LA)	*n*-butanol (8, 16)	No	LSD	▲:UHC ▼:Smoke, NO_x, CO	▲:BSFC, BTE	Engine speed and load
Yao et al. [180]	Turbo charged inter-cooled HDDI diesel engine	*n*-butanol (5, 10, 15)	No	Diesel	▼:Soot, CO, THC	—:BSFC	Multi-injection timing, EGR
Al-Hasan et al. [181]	Single cylinder 4-stroke CI diesel engine (Lister 8-1 TE 9)	*iso*-butanol (10, 20, 30, 40)	No	Diesel	n/a	▲:BSFC ▼:BTE, Brake power, $T_{exhaust}$ ▲: Brake power[a], $T_{exhaust}$[a]	Engine speed and load
Karabektas et al. [182]	Single cylinder DI diesel engine	*iso*-butanol (5, 10, 15, 20)	No	Diesel no. 2	▲:HC ▼:CO, NO_x	▲:BSFC ▼:BTE, Brake power	Engine speed
Asfar et al. [183]	Single-cylinder 4-stroke water-cooled, CI engine	*iso*-butanol (5,10)	10	Diesel fuel	▼:NO_x, Soot, CO, UHC —:CO_2,CO	▲:BSFC	–
Ozsezen et al. [184]	6-cylinder TDI (heavy-duty) diesel engine	*iso*-butanol (5,10, 15)	No	Euro class diesel	▲:HC ▼:NO_x, Smoke, CO	▲:BSFC ▼:BTE, Brake power	Engine load and speeds
Biao et al. [185]	High-speed inter-cool heavy-duty diesel engine	*n*-butanol (20, 30)	No	Diesel	▼:Soot	▲:BSFC	*n*-butanol ratio, engine speed
Dogan et al. [186]	Single cylinder 4-stroke naturally aspirated DI diesel engine	*n*-butanol (5,10, 15, 20)	No	LSD	▲:HC ▼:NO_x, CO, Smoke	▲:BSFC, BTE ▼:$T_{exhaust}$	Engine load
Rakopoulos et al. [187]	Single cylinder 4-stroke water-cooled (Ricardo/Cussons P8800 'hydra') DI diesel engine	*n*-butanol (8,16, 24)	No	LSD	▼:NO_x, CO, Smoke	▲:Ignition delay, fuel injection pressure ▼:Cylinder temperature	Engine load
Yao et al. [194]	Single cylinder 4-stroke water-cooled diesel engine	*n*-butanol (10, 20)	No	Diesel	▼:NO_x, Soot —:CO,THC	▲:Ignition delay	EGR, injection pressure and timing
Tornatore et al. [195]	Single cylinder 2-stroke high pressure common rail CI engine	*n*-butanol (20)	No	LSD	▼:NO_x, Smoke	▲:Ignition delay	EGR, injection time and pressure
Yoshimoto et al. [196,197]	Single cylinder 4-strokeDI diesel engine	*n*-butanol (9, 17, 23, 29, 33, 43, 50)	1	Biodiesel and gas oil	▼:Smoke —:$NO_x$$NO_x$	▲:BSEC	–
Lujaji et al. [198]	4-cylinder TDI diesel engine	*n*-butanol (5, 10)	10 15	Diesel No.2	▼:CO_2, Smoke —:NO_x	▲:BSEC ▼:BSFC	–
Altun et al. [199]	Single cylinder 4-stroke naturally aspirated DI compression ignition engine	*n*-butanol (10, 20)	20	Diesel	▼:CO, HC NO_x	▲:BSFC, BTE	Engine load
Rakopoulos et al. [200]	Mercedes-Benz OM 366 LA after-cooled TDI diesel engine	*n*-butanol (25)	No	LSD	▼:Smoke ▲:NO	▼:cranking speed	Biodiesel (50%)
Rakopoulos et al. [201]	Mercedes-Benz OM 366 LA after-cooled TDI diesel engine	*n*-butanol (25)	No	LSD	▲:NO ▼:Smoke	n/a	Biodiesel, engine load

▲, Increase; ▼, Decrease; —, no change; n/a, not available.
[a] at high engine speed.

CN compared with diesel fuel. However, low CN may be needed in future diesel combustion processes to increase the auto ignition delay and premixed combustion, thereby reducing soot emissions.

Based on these reviews, the studies of butanol/*iso*-butanol in diesel engines have been limited therefore, more studies of butanol to examine following aspects of its use:

(i) Experimental work related to the stability of butanol–diesel blend fuels and their effects on performance, emissions and combustion should be carried out in DI engines at high and low temperatures (-10, -25 °C).
(ii) The roles of different additives (i.e., CN improver) in butanol or *iso*-butanol–diesel blends should be studied in terms of fuel properties, combustion, performance and emissions.
(iii) The best butanol content in fuel blends should be identified in order to optimize functionality as an alternative fuel.
(iv) As in methanol and ethanol–diesel fuel blends, fuel injection techniques such as fumigation and dual fuel injection should be used with butanol diesel blends to better control emissions and to enhance engine performance.
(v) The effects of injection timing and pressure on the emissions and performance should be investigated for butanol–diesel blends.
(vi) EGR is an important parameter for controlling diesel engine combustion, performance and emissions, especially NO_x and soot emissions. Few studies have examined this parameter [188], and therefore more extensive studies are recommended.

6. Conclusions and future research directions

Continuous dependence on fossil fuel energy resources is unsustainable, due to both the depletion of global reserves and threatening greenhouse gas emissions associated with their use. Explorations of alternative fuels as full or partial replacements for diesel fuels have become globally critical in order to ensure future environmental security. Bio-alcohols such as methanol, ethanol and butanol have appeared as one of best alternative and sustainable fuel sources, and are considered as a potential solution to alleviating greenhouse gas emissions. Due to their large scale production from cellulosic biomass instead of food grains using advanced biotechnological techniques and comparable fuel properties with fossil fuels, these alcohols are considered as high quality fuels. These can be either blended with diesel fuels or used in neat form in diesel engines without any further modifications. Further, these alcohols may reduce engine emissions as they have lower carbon and sulfur contents, and higher oxygen content than fossil fuels. Thus, alcohols can reduce our dependence on fossil fuels as energy sources for vehicles.

Therefore, intensive investigations are recommended to examine the effects of alcohol–diesel blends on the performance, emissions and combustion behaviors of diesel engines. Major technological innovations and policy changes are required to facilitate the extraction of biofuels from cellulosic biomass to increase the value of biofuels as alternatives to traditional fossil fuels. One of the biggest problems with cellulosic biofuels is cost. Research for the development of less expensive and/or more efficient enzyme conversion technologies to harness biofuels from cellulosic biomass is warranted.

Butanol has a number of advantages over ethanol and methanol as an alternative fuel for IC engines, since many of the fuel properties of butanol are more similar to those of fossil-based fuels than are those of ethanol or methanol. Butanol also has high CN, low vapor pressure, and high miscibility which make it a more suitable additive to diesel fuel than ethanol or methanol. Butanol is less corrosive and has higher energy content than ethanol or methanol. Therefore, butanol is a better component for use as a fuel additive to hydrocarbon fuels than other alcohols. Hence, branched chain higher alcohols (such as *iso*-butanol, 1-butanol, 2-methyl-1-butanol, 3-methyl-1-butanol, 2-phenylethanol) should be synthesized as compared to lower alcohols because of their high energy density and low hygroscopicity, and their applications in diesel engines should be assessed.

The literature reported in this article indicates that smoke density, CO and THC emissions decrease while NO_x emissions increase; however, NO_x emissions decrease and hydrocarbon emissions increase as butanol content in fuel blends increases. In an equimolar comparison of *n*-butanol and *iso*-butanol, *n*-butanol–diesel fuel blends resulted in increased BTE and BSFC, and decreased exhaust gas temperature. In contrast, *iso*-butanol–diesel fuel blends resulted in increased BSFC but reduced engine power, BTE and exhaust gas temperature. In addition to the amount of alcohol in the diesel alcohol blend, the fuel injection system used has been found to play an important role in reducing emissions to acceptable levels. Increasing the injection pressure reportedly increases NO_x emissions while decreases the smoke opacity. The injection timing also affects engine performance and exhaust emissions from diesel engines. Further, some new fuel injection techniques should be developed in order to enhance diesel engine performance and reduce emissions.

In conclusion, alcohol–diesel fuel blends reduce the engine emissions without serious impacts on engine performance. Fuel additives and CN improvers were found to enhance the fuel properties and stability of blends. Further experimentations, mainly at low temperatures, are required to identify the optimum percentages of alcohols for use in alcohol–diesel blends, to assess stability of the alcohol–diesel blends, and to understand the roles of different additives to improve the potential for alcohol–diesel fuel blends (especially higher alcohols) to be used as next generation fuels.

Acknowledgments

This research was supported by a grant from the GAS Plant R&D Center funded by the Ministry of Land, Transportation and Maritime Affairs (MLTM) of the Korean government and the Ministry of Education (MOE) of Korea through its BK21 Program.

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